

Bulletin 1

DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

JOSEPH A. HOLMES, DIRECTOR

THE VOLATILE MATTER OF COAL

BY

HORACE C. PORTER

AND

F. K. OVITZ



WASHINGTON
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THE VOLATILE MATTER OF COAL.

By HORACE C. PORTER and F. K. OVITZ.

INTRODUCTION.

SCOPE OF REPORT.

The various fuel investigations that were being carried on by the technologic branch of the United States Geological Survey were transferred by law on July 1, 1910, to a new federal bureau, the Bureau of Mines, that was authorized to continue the investigations and make public reports of the results. In consequence of this transfer, the following report is published as a bulletin of the new bureau.

The United States Geological Survey had been engaged in analyzing and testing coals, lignites, and other mineral fuel substances under authority given by act of Congress. This work, now centered at the experiment station at Pittsburgh, Pa., had its beginning in the operations of the coal-testing plant erected at the Louisiana Purchase Exposition in St. Louis, Mo., in 1904. The results obtained at that plant showed that the work of determining the fuel value of the coals and lignites in the United States with a view to increasing efficiency in their utilization would be incomplete if it did not include systematic physical and chemical researches into the processes of combustion. Hence in its later investigations the Survey carried on such researches, concentrating attention on those lines of inquiry which promised results of greatest economic importance.

This bulletin is a report on an investigation of the volatile matter in several typical coals—its composition and amount at different temperatures of volatilization. As the investigation is still in progress and will doubtless include other coals than those already examined, the bulletin may be considered a preliminary report, stating the problems studied, the methods used, and the results thus far obtained.

SUMMARY OF RESULTS.

The investigation has already shown that the volatile content of different coals differs greatly in character. The volatile matter evolved from the younger coals of the West includes a large proportion of

carbon dioxide, carbon monoxide, and water, and a correspondingly small proportion of hydrocarbons and tarry vapors. The older bituminous coals of the Appalachian region yield volatile matter containing large amounts of tarry vapors and hydrocarbons, difficult to burn completely without a considerable excess of air and a high temperature. Coal of the western type, moreover, gives up its volatile matter more easily at moderate temperatures than coal of the eastern type. The volatile matter produced at medium temperatures is rich in higher hydrocarbons of the methane type, such as ethane and propane, which contain a larger proportion of carbon than is present in methane. These facts help to explain the difficulty of burning Pittsburgh coal, for example, without smoke, the low efficiency usually obtained in burning high-volatile western coals, the advantage of a preheated auxiliary air supply introduced over a fuel bed, and the advantage of a furnace and boiler setting adapted to the type of fuel used. They bear directly also on the question of steaming "capacity" of coals for locomotives, the designing and operation of gas producers for high-volatile fuels, and the operation of coke ovens and gas retorts.

The results show further that certain bituminous coals of the interior and Rocky Mountain provinces give promise of good yields of by-products of coking, notably ammonia and high-candlepower gas, comparing favorably in these respects with the high-grade coking coals of the eastern province.

They show also that inert, noncombustible material is present in the volatile products of different kinds of coal to an extent ranging from 1 to 15 per cent of the coal.

DEFINITION OF VOLATILE MATTER.

The term "volatile matter" in coal, as distinguished from the term "volatile combustible matter," may be criticized on the ground that moisture is volatile and would therefore by implication be included in the term "volatile matter." On the other hand, the present investigation shows that the volatile matter exclusive of "moisture" contains considerable percentages of noncombustible materials, such as carbon dioxide, water, and nitrogen, and the application of the term "combustible" is therefore hardly justifiable. Less confusion seems likely to result from designating the volatile matter exclusive of moisture "volatile matter," even though moisture is also volatile, than would result from applying the term "combustible" to material which is one-tenth to one-third noncombustible.

OBJECT OF INVESTIGATION.

Methods for the quantitative estimation of volatile matter have not entered into the present investigation, the object of which has been rather to determine the composition of the volatile matter evolved at

different temperatures from different types of coal and to show the influence of this factor on efficiency in the use of coal.

BEARING ON BOILER-FURNACE OPERATION.

If a furnace produces 15 pounds of flue gases from 1 pound of fuel, and if these gases, by reason of improper firing or furnace setting, contain unconsumed combustible gases to the extent by volume of 0.5 per cent of CO, 0.5 per cent of H, and 0.4 per cent of CH₄, the theoretical loss through these materials is approximately 10 per cent of the heating value of the coal. For every 0.1 per cent of CO in the flue gas the efficiency is lowered theoretically 0.47 per cent; for 0.1 per cent of H, 0.48 per cent; and for 0.1 per cent of CH₄, 1.52 per cent.

In the report entitled "A study of four hundred steaming tests"^a it is shown that in 48 tests made at the St. Louis fuel-testing plant of the Geological Survey, as the CO in the flue gas increased from 0.3 to 0.7 per cent the efficiency dropped from 65 to 57 per cent—about 2 per cent for each 0.1 per cent of CO, or four times the above-stated theoretical drop. The amounts of H and CH₄ in the flue gas were not determined in these tests. In the discussion of the relation between efficiency and CO, however, the following statement is made: "We therefore reach the inevitable conclusion that at least two-thirds of the large drop in code 'boiler efficiency' with rise of CO is due to incomplete combustion losses not represented by CO, so that high CO is a decided danger signal." Very few records of determinations of hydrocarbons or hydrogen in flue gases are to be found, presumably because of the analytical difficulty in determining such small quantities. In the report of the Manchester (England) Smoke Committee, 1895,^b are given some flue-gas analyses showing in certain tests of hand-fired furnaces 0.25 to 0.40 per cent of CH₄ and 0 to 1 per cent of H. Recent tests at the Geological Survey's plant on small house-heating boilers using Pittsburgh slack coal have given in the flue gases as high as 2.8 per cent of CO and nearly 1 per cent each of H and CH₄, the conditions in these tests being, however, extremely unfavorable to complete combustion and not parallel to those in larger plants. There seems to be a strong probability, nevertheless, that in the greater number of smoking chimneys volatile combustible gases are escaping which carry from 3 to 10 per cent of the total heat value of the fuel; and it is easy to see the importance of improving methods for the analytical determination of methane and hydrogen in flue gas and of devising a method whereby samples may be taken which are less diluted with air, in order that the CO, CH₄, and H may appear as larger percentages.

^a Bull. U. S. Geol. Survey No. 325, 1907, pp. 28, 65.

^b Cited in Bull. U. S. Geol. Survey No. 334, 1908, p. 14.

E. J. Constam and P. Schläpfer,^a in an extended series of boiler trials of European coals, using the internally fired marine type of boiler, have shown in a striking manner the effect of the amount and composition of the volatile matter on the boiler efficiency. They found in the flue gas from one coal 3.5 per cent of CO, and 1.5 per cent of H, which caused an efficiency loss of 17.2 per cent.

Several factors may enter into the unaccounted-for losses in the heat balance of a steaming test. For example, it is likely that more heat is carried away by the flue gases (including steam) than is usually charged to them, for the reason that their specific heat probably increases with temperature; and this factor is of special importance for low-grade, high-moisture, high-oxygen coals. Another factor is the loss of solid combustible material in the chimney gas, or "spark-ing," which also is more prevalent with low-grade fuels. That the most important "unaccounted-for loss," however, is likely to be found in the unburned volatile gases which are allowed to escape through lack of sufficient combustion space or of a sufficient supply of heated air, the above considerations are intended to show. The present paper confirms and explains the known facts that in order to obtain high efficiency the furnace must be adapted to the fuel and that the character, as well as the amount, of volatile products is of decided importance. The following results of steaming tests made at the Geological Survey's plant, compared with some results from the present investigation on the character of the volatile matter in the coals used, will further illustrate this point:

TABLE 1.—*Steaming tests of various coals.*

Coal No.	Volatile matter in dry coal (per cent).	Combustible gas at 600°. ^a	Heavy hydrocarbon gases at 600°. ^a	Steam test No.	Boiler efficiency (per cent).	Unaccounted-for loss (per cent).	CO in flue gas (per cent).	Rate of firing. ^b
W. Va. 11.....	20.8	60	5.6	56	68.3	5.4	0.05	18.1
Pa. 19.....	32.9	498	63.9	8.7	.04	20.4
				308	65.6	7.1	.02	21.0
Lab. 3.....	30.4	75	8.5
Ill. 19.....	33.0	108	10.5	160-63	63.7	12.5	.19	19.0
W. Va. 13.....	32.6	116	13.8	179-80	68.1	11.1	.14	15.7
Wyo. 4.....	45.4	399	56.4	15.9	.07	24.0
Lab. 18.....	43.4	142	19.4
Wyo. 1.....	43.8	165	15.1	63	54.9	11.2	.25	22.7
				291	59.9	6.9	.0	23.1
Tex. 4.....	41.6	298	51.2	17.6	.0	35.2

^a Volume in cubic centimeters from 10 grams in ten minutes, laboratory test.

^b Pounds of dry coal per square foot of grate surface per hour.

W. Va. 11. Pocahontas bed, "smokeless" coal.

Pa. 19. Pittsburg bed, Westmoreland County.

Lab. 3. Pittsburg bed, Connellsville, Fayette County, Pa., similar to Pa. 19.

Ill. 19. No. 7 seam, Zeigler, Franklin County.

W. Va. 13. "No. 2 gas coal," Page, Fayette County.

Wyo. 4. Bituminous coal, Hanna, Carbon County.

Lab. 18. Bituminous coal, Diamondville, Uinta County, Wyo., somewhat similar to Wyo. 4.

Wyo. 1. Subbituminous, Sheridan district, 22 per cent moisture.

Tex. 4. Lignite, Wood County, 36 per cent moisture.

Inasmuch as the values given for unaccounted-for losses in a steaming test embody all the errors of the other determinations, little dependence can be placed on any relation shown under that heading. The relations shown, however, under boiler efficiency, CO, and rate of firing, as compared to ease of liberation of volatile gases, are instructive. Wyo. 1, for example, compared with W. Va. 11, was burned with low efficiency, high CO, and high unaccounted-for loss, while in the laboratory test its gases were liberated much more easily. The rate of firing is an important factor. Coals of low heating value must be fired at a high rate in order to maintain a given boiler capacity, and as these coals are commonly high in volatile matter, the danger of loss of volatile gases is correspondingly great. W. Va. 13, in the table above, was fired at a low rate, which may account for the fact that it shows high efficiency, even though its volatile gases are easily liberated.

BEARING ON SMOKE PRODUCTION.

Visible smoke consists of solid carbon particles and solid or liquid hydrocarbon particles or "tar vapors." Both result from incomplete combustion of the volatile products of the fuel. The carbon of the smoke is not derived from free carbon in the fuel, but is deposited by the cooling of hot dissociated hydrocarbon gases. Flame is a phenomenon accompanying the chemical union of certain gases, one of which is usually oxygen;^a and the incandescent particles make a flame visible. If some of these particles in the flame are carbon, formed by the dissociation of hydrocarbons, luminosity results; and if the temperature of these particles is reduced below the point at which they combine with oxygen, or if sufficient oxygen is not at hand to effect the union, they fail to unite with oxygen and pass off as solid carbon in smoke. These principles are stated very clearly by L. P. Breckenridge in "How to burn Illinois coals without smoke."^b When a coal produces rich volatile gases, bearing large amounts of heavy hydrocarbons, a comparatively large combustion space must be provided to allow the flame to be burned out before striking cool surfaces; and the flame must have an adequate supply of air at an adequate temperature if it is to be burned out in time. Furthermore, when rich volatile products distill rapidly from a coal at medium and low temperatures, they must be taken care of by increased combustion space or by decreased rate of firing. The essential requirements of smokeless combustion are therefore three: (1) Sufficient combustion space, (2) sufficient air at a high temperature, and (3) sufficient thorough mingling of gases and air—these three conditions to be adapted to the type of fuel and the nature of its volatile products. Tabulated data and comparisons are given elsewhere in this paper (pp. 32–40) which bear upon the smoke-producing tendencies^c of the coals tested.

^a Lewes, V. B., The luminosity of coal-gas flames: Proc. Roy. Soc., vol. 57, 1895, p. 450.

^b Bull. 15, Univ. Illinois Eng. Exper. Sta., p. 7.

^c See Addenda, p. 56.

BEARING ON LOCOMOTIVE FIRING.

For locomotive use that coal is most desirable which will give the highest boiler efficiency when burned so as to produce the required high evaporative rate (11 to 14 pounds of water per square foot of boiler heating surface per hour). Reduction of boiler efficiency under these conditions may be due to several causes, chief among them being loss of sensible heat, loss of cinders, and loss of combustible gases through the stack. That the last-named factor is of large influence it seems safe to conclude from the general rule that high rate of firing involves increase of unconsumed combustible gases in the flue gas. In view of the high rate of firing and the small combustion space in a locomotive, the bearing of the nature of the volatile products of the fuel on the completeness of their combustion under these unfavorable conditions may readily be seen.

BEARING ON GAS-PRODUCER, COKE-OVEN, AND GAS-RETORT OPERATION.

At the top of the fuel bed in a gas producer the volatile products of the fuel are distilled. In many types of producer these products are distilled at medium and low temperatures, and those of some high-volatile fuels contain such large amounts of tar and heavy hydrocarbons that it is necessary to draw them downward through the hot fuel and convert them into permanent gases in order to avoid losses through the deposition of tar and soot. The value of a knowledge of the nature of the volatile products from different fuels is evident.

The carbonization of coal in coke ovens and gas retorts is chemically an exceedingly complex process. It involves the distillation of volatile products at all temperatures from 100° to 1,200° C. The composition of the final volatilized product is determined not only by the temperature within the distilling substance, but also more largely by the temperature of the region through which the products pass. This composition is a resultant of the distillation of many coal particles, each probably at a different temperature, and of the time and temperature conditions to which the first products are subjected after leaving their original state of combination in the coal substance. The bulk of the mass heated and the rate of supply of heat from without determine the time and temperature conditions to which the products are subjected. In the study of industrial coal-carbonization processes, coke ovens, horizontal gas retorts, and vertical retorts, therefore, a knowledge of the variation among coals in the nature of their resultant volatile products at different maximum temperatures should aid in fixing the most favorable working conditions. The results presented in this paper show that the first products when coal is gently heated without access of air are CO₂,

and saturated paraffin hydrocarbons. From coking and gas coals the latter are formed in abundance, and it is from their decomposition at high temperatures that the various constituents of coal gas and coal tar are formed. Highly oxygenated coals produce large quantities of CO_2 and CO .

NATURE OF COAL SUBSTANCE.

The products of the thermal decomposition of certain types of chemical compounds are known, and thus by a study of destructive distillation an insight may be gained into the chemical nature of coal. A more promising method of attacking the problem seems to be that of extraction with solvents or modification of the substance by treatment with chemical reagents, together with systematic microscopical examination. Such investigations are now being carried on in the laboratories of the Bureau of Mines. It is hoped that with the results of these studies the data on destructive distillation afforded by the present investigation may be coordinated in such a way as to aid in throwing light on the problem.

EFFECT OF OXYGEN IN COAL ON CALCULATION OF HEAT VALUE FROM ULTIMATE ANALYSIS.

Oxygen, as well as ash, moisture, and nitrogen, exercises an anti-calorific influence on coal. Not only is it a diluent, or so much "dead weight," like the other three constituents mentioned, but it also neutralizes or renders ineffective an equivalent combining weight of carbon, hydrogen, or sulphur. In some coals this neutralizing action may be accompanied by the development of heat, for it is known that in destructive distillation exothermic reactions take place.^a But oxygen is nevertheless in combination in the coal substance and must therefore be considered as rendering inert a certain portion of the fuel elements. In all the applications of fuel the first stage in the decomposition is probably the distillation of the volatile products, and as hydrogen has a higher calorific value than an equivalent weight of carbon, the distribution of oxygen between carbon and hydrogen in the volatile products has a direct influence on the calorific value of the fuel. Available hydrogen has greater value than available carbon. P. L. Dulong's method of calculating heat value reduces the available hydrogen by the amount which would combine with all the oxygen, and therefore gives too low a value in coals which distribute a large proportion of their oxygen to carbon rather than to hydrogen. The experimental results given in this paper show that in certain low-grade, highly oxygenated coals nearly two-thirds of the oxygen

^a Constam, E. J., and Schl pfer, P., Jour. Gasbel., 1906, pp. 741, 774.

appears in the volatile products in union with carbon, and that this accounts largely for the difference between the determined heat value and that calculated by Dulong's method. (See pp. 42-44.)

RELATED INVESTIGATIONS BY OTHERS.

E. Börnstein^a has carried out elaborate experiments on the distillation of German bituminous and brown coals at temperatures up to 450° C. He obtained tars with no solid aromatic hydrocarbons and gases containing large amounts of CO₂ and homologues of methane.

E. J. Constam and E. A. Kolbe^b distilled at high temperatures a number of bituminous coals of varying composition and obtained from those high in oxygen large amounts of CO₂ and CO and correspondingly less amounts of hydrocarbons.

L. Vignon^c distilled at 900° C. five coals of varying known oxygen content and attempted to establish a ratio between the amount of the oxides of carbon and the oxygen in the coal.

S. W. Parr and C. K. Francis^d have distilled Illinois coal (4 to 5 pounds) at 200° to 425° C. for two to three hours in an inert atmosphere and obtained from 3 to 4.5 per cent of water of composition, a small amount of oil, and 600 to 700 cubic feet per ton of gas high in CO₂, illuminants, and "methane." Homologues of methane are not mentioned in the report of this work, but are probably included under "methane."

A. H. White, F. E. Park, and W. A. Dunkley,^e have studied the low-temperature distillation of three typical American coals and its bearing on the manufacture of illuminating gas. They distilled 50 to 75 grams for six to eight hours at 300° to 500° C. and obtained small quantities of liquid and oily distillates with 1,200 to 2,800 cubic feet per ton of gas rich in methane and ethane. The following tabulated statement of results is given:

TABLE 2.—Gas obtained by distillation of three typical American coals.

Volume and composition of gas.	Pitts- burgh, Pa.	Bay City, Mich.	Zeigler, Ill.
Volume of gas (cubic feet per pound of coal).....	1.42	1.15	0.63
Average composition of gas:			
CO ₂	2.9	16.2	13.1
Illuminants.....	2.2	4.1	1.6
CO.....	6.2	5.0	5.8
H.....	26.3	16.4	13.9
CH ₄	47.0	37.8	38.0
C ₂ H ₆	13.2	11.8	19.5
N.....	2.7	9.1	7.8

^a Zeltschr. angew. Chemie, vol. 17, 1904, p. 1520; Jour. Gasbel., vol. 49, 1906, pp. 627, 648, 667; Jour. Soc. Chem. Ind., vol. 25, 1906, pp. 213, 583.

^b Jour. Gasbel., vol. 51, 1908, p. 669.

^c Bull. Soc. chim., 4th ser., vol. 3, 1908, p. 109.

^d Bull. 24, Univ. Illinois Eng. Exper. Sta., 1908; Trans. Am. Inst. Min. Eng., 1908, p. 1158.

^e Am. Gas Light Jour., vol. 89, 1908, p. 621.

The heating power of the solid residue was greater than that of the coal, but the coking property was destroyed. The manner and the points of temperature measurement are not stated.

R. T. Chamberlin, of the United States Geological Survey, has made a study ^a of the gases liberated from coal at ordinary temperature and of those evolved from coal dust at somewhat higher temperatures (200° to 450° C.). He ascribes the evolution of gas that occurs at 450° largely to chemical changes in the coal substance rather than to liberation of imprisoned gas. The gas at 450° consisted of 60 to 70 per cent of methane, 12 to 18 per cent of ethane, 5 to 6 per cent of heavy hydrocarbons (benzene, ethylene, etc.), and small percentages of carbon dioxide, carbon monoxide, and sulphurous gases. Chamberlin's results are applied to an investigation of the causes of mine explosions and to the method of accumulation of gas in mines. At temperatures below 350° he obtained only very slight percentages of ethane in the gas, and concludes that in the imprisoned gases of the coals studied (Pennsylvania and West Virginia) ethane is not present to any appreciable extent.^b

EXPERIMENTAL PLAN OF PRESENT INVESTIGATION.

It has been the plan in the present investigation to extend such studies as those described above to several types of American coals and to a greater variety of experimental conditions of such kind as to indicate the behavior of these coal types in their industrial applications. It has been borne in mind throughout that industrial conditions can scarcely be duplicated in the laboratory, and that any selected set of laboratory conditions (of temperature and of quantity, for example) must be considered as corresponding to merely a part of the varied conditions that may exist simultaneously in an industrial practice. The laboratory method, however, permits more exact measurements and presents the further advantage that a few definite and controllable conditions can be selected from among the many indefinite ones of industrial practice, and their effect determined with more certainty. It is not claimed that the experimental data of this investigation show absolute industrial yields either in quantity or in composition of products, but it is held that they afford a comparison of various coals under fixed conditions, and also that they justify conclusions as to the probable industrial behavior of the different coals, in furnace, coke oven, or producer.

^a Notes on explosive mine gases and dusts: U. S. Geol. Survey Bull. No. 383, 1909.

^b After the publication of the first edition of Bulletin 1, Bureau of Mines, there appeared in the Journal of the Chemical Society (London), vol. 97, p. 1917, and vol. 99, p. 649, two articles by M. J. Burgess and R. V. Wheeler on "The Volatile Constituents of Coal," describing an investigation similar to that described here. For the results of still later investigations, see "The Coking of Coal at Low Temperatures," by S. W. Parr and H. L. Olin. Bull. 60, Univ. Illinois Eng. Exper. Sta., 1912.

For comparing coals as to the composition and the rate of formation of their volatile products at a number of given temperatures, 10-gram samples of air-dried powdered coal were heated in an inert atmosphere in a platinum retort. For comparing coals as to their yields of by-products of coking, under one given set of conditions approximating those of industrial practice, tests were made on 400-gram samples of crushed coal as received, heated in a cast-iron retort. Direct weighing of tar and of water of composition and the determination of ammonia were capable of greater accuracy in the 400-gram tests than in the 10-gram tests. Nine different coal types were used, ranging from a low-grade subbituminous coal from Wyoming to the high-grade Connellsville and Pocahontas coals of the Appalachian region.

METHODS.

COLLECTION AND PREPARATION OF SAMPLES.

The samples of coal used in these investigations were with one exception mine samples collected by representatives of the United States Geological Survey in the manner prescribed for the work of the fuel-testing plant.^a The one exception was coal No. 23 from a mine near Harrisburg, Saline County, Ill., this sample being a car sample of screened coal (2-inch to 3-inch size) taken by a representative of the Illinois State Geological Survey from a car at the mine, one day after it had been mined.

Samples of about 100 pounds each, representing the entire seam as mined, were shipped to the laboratory in canvas bags or (in case of coals particularly subject to deterioration from exposure) in tightly closed kegs or barrels.

At the laboratory the entire sample was crushed to $\frac{1}{2}$ -inch size and a portion of 8 to 10 pounds was taken by quartering for air drying. From this air-dried portion a 500-gram sample was taken by quartering, pulverized to 60-mesh size in the closed ball mill, and bottled in a "lightning" fruit jar for analysis. The bulk of the original sample was placed in a galvanized ash can having a tightly fitting cover, and the portion of the air-dried sample not pulverized was placed in a tin milk can with a tight cover sealed with tape. The time that elapsed between mining the coal and placing it in covered containers varied from three to five weeks; during this time there was undoubtedly some loss in mine moisture and possibly slight changes in the coal substance due to oxidation. The subbituminous coals, however, which are high in moisture and more subject to change, were kept in tightly closed kegs and probably changed very little.

^a Bull. U. S. Geol. Survey No. 290, 1906, p. 17.

The proximate analyses and sulphur, nitrogen, and calorimetric determinations were made on the air-dried powdered samples according to the methods of the fuel-testing plant.^a

TESTS IN IRON RETORT.

APPARATUS.

For the purpose of comparing coals in respect to their yields of by-products of coking as well as the composition of their volatile products, a cast-iron retort holding somewhat less than a pound of coal was used, together with apparatus as illustrated in Plate I, *A*.

The bottles *a*, *b*, *c*, and *d* contain dilute sulphuric acid; the tower *e* and condenser *f* contain glass beads over which water flows from the funnel *g*; the upper portion of *f* contains absorbent cotton to collect the last traces of tar. It was found by placing two drops of normal acid in *d*, with a little cochineal as indicator, that no ammonia passed through the acid in *c*. The bottle *h* contains 30 per cent potassium hydroxide solution and the tower *i* holds glass beads wet with the same solution from funnel *j*. The gages *k* indicate the gas pressure at the beginning and end of the train. Temperatures in the furnace and inside the iron retort were read by means of thermocouples connected through a cold junction bath (*l*) and switch to the millivoltmeter (*m*).

Figure 1 shows a vertical section through the furnace viewed from the side. This furnace was designed and constructed on the plan of those used by A. L. Day in the geophysical laboratory of the Carnegie Institution, Washington, D. C.^b The outer cylindrical jacket (*A*) is of ordinary fire clay and the inner one (*C*) of "magnesite," a highly refractory material composed chiefly of magnesium oxide. The inner cylinder rests upon small fire-clay blocks, and the space (*B*) between the two cylinders is filled with light calcined magnesia. For convenience in winding the heating coils, the inner cylinder is in two sections placed end to end. The heating coils (*D*) are of pure nickel wire, No. 13 Brown & Sharpe gage, and are cemented to the inside of the inner cylinders by means of "magnesite" powder wet with water and a little gum tragacanth. The strands of wire are about 2 millimeters apart. For winding the coils a cylindrical arbor of hard wood is used, which is slightly smaller than the inside diameter of the furnace and is made up of wedge-shaped sections, so as to be collapsible and readily removed. The arbor, after being covered with paper, is wound with the wire, coated with cement, and placed in the furnace cylinder, and the annular space is packed with cement. After drying thoroughly, the arbor is removed and a final surface layer of cement is coated over the coils.

^a Prof. Paper U. S. Geol. Survey No. 48, 1906, pp. 178-190.

^b Day, A. L., and Allen, E. T., Am. Jour. Sci., 4th ser., vol. 19, 1905, p. 93.

A furnace made thus with nickel wire stands from 50 to 75 heats at $1,100^{\circ}\text{C}$. without renewal of the coils. The cement covering of the coils must, however, be kept intact by frequent patching to insure long life of the wire. A direct current of 220 volts was used, the strength varying from 18 to 25 amperes according to the variation of the resistance with the temperature.

Figure 1 shows also a vertical section of the iron retort viewed from the side. When the inside thermocouple is used, the coke is conveniently added through the delivery pipe after the pipe is screwed in

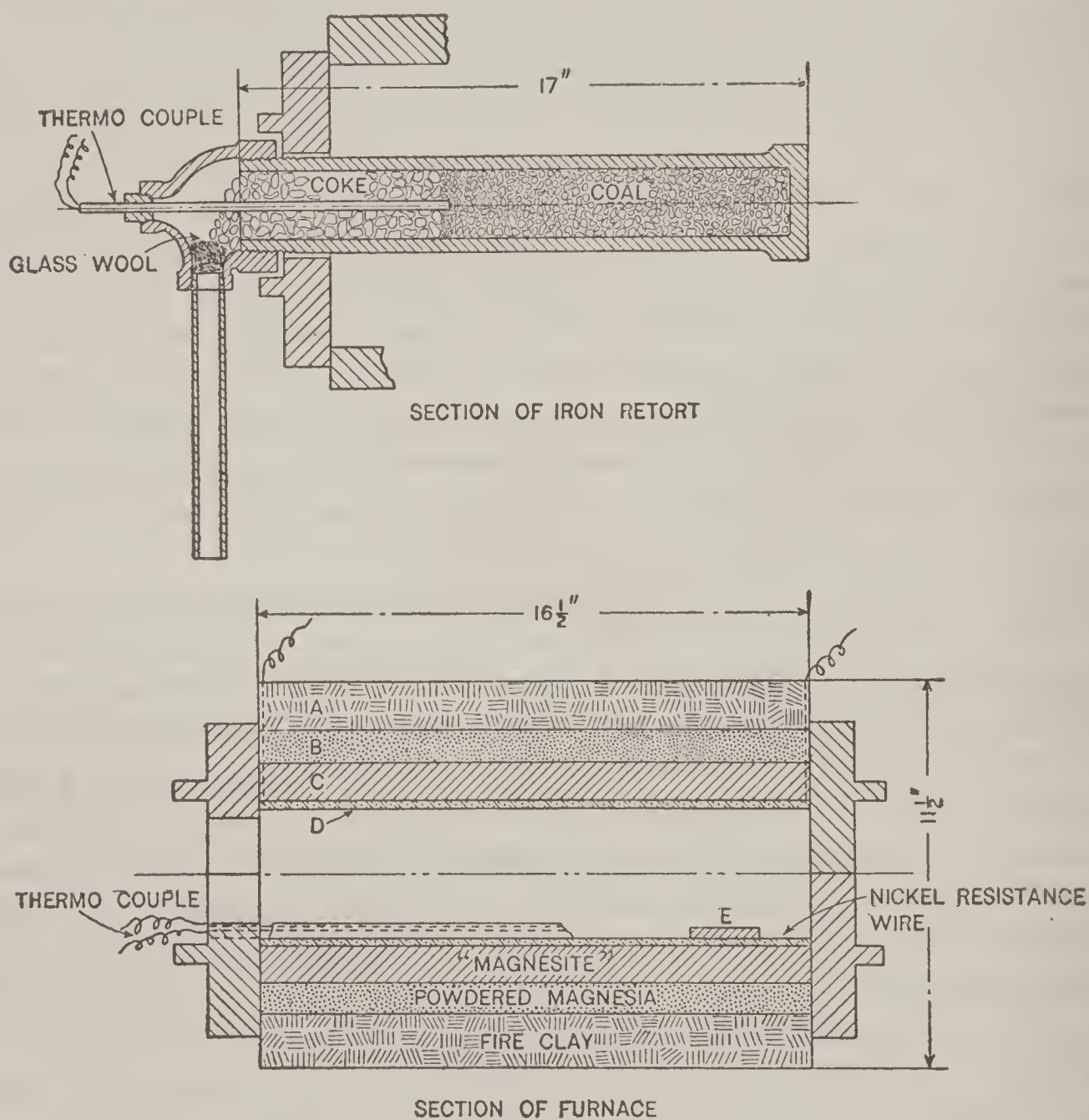


FIGURE 1.—Section of iron retort and section of large electric furnace.

place. The retort burns away on the surface and can be used for only 6 to 8 heats at $1,100^{\circ}$.

It was found impracticable to have the threaded joint of the retort inside the furnace and maintain it gas tight or to constrict the neck of the retort near the joint because of difficulty in removing the coke. If the threads are well made and kept lubricated with graphite there is no difficulty in keeping the joint gas tight. The walls of the retort were made heavy (one-half inch) so as to withstand better the scaling effect of the high heat. The conditions as to rate of heating

were therefore somewhat different from those of a coke oven or gas retort where the coal is charged directly into the heated chamber. The difference, however, is due more to loss by radiation through the large exposed surface of the retort outside of the furnace than to the presence of the iron wall between the coal and the furnace. The iron wall of the retort transmits heat to the coal rapidly, being a better conductor of heat than the layer of partly coked coal which forms next to the walls of a coke oven when the charge is introduced. The temperature less than 4 inches from the wall of a retort coke oven has been found to remain below 200° C. for five hours after charging.

The radiation, however, from the front and neck of the iron retort lowers the temperature of those portions to such a degree that tar vapors and heavy hydrocarbon gases pass through with less breaking down than in coke ovens or gas retorts; consequently the yields of tar and heavy paraffin hydrocarbons are greater in the laboratory tests than in commercial practice. The front part of the retort is filled with coke, in pieces of about $\frac{1}{2}$ -inch size, for the purpose of preventing the crowding forward of coal and tar. This coke does not become hotter than 600° C., on account of the cooling effect of radiation on the front of the furnace and retort. It is important to have the coal occupy the same space in the retort and be in the same relative position in the furnace in all tests, for the gas yield is materially influenced by these conditions.

The thermocouples and millivoltmeter used were standardized at the beginning of the investigations by the Bureau of Standards, Washington, D. C., and found to be correct within 5° C. at temperatures between 400° and 1,600° C., the cold junctions being at 25° C. They were standardized also after the completion of these investigations, at the physical laboratory of the Bureau of Mines, by means of the melting points of pure zinc and pure copper, and were again found correct within the limit mentioned.

The gas meter used (*p*, Pl. I, *A*) was Goodwin's experimental gas meter of 0.1 cubic foot capacity per revolution, furnished by the American Meter Company. The correct water level in the meter was established by aspirating about 0.5 cubic foot of air through the meter and determining its volume by the weight of water displaced in the aspirator bottles. For collecting the gas a 55-gallon barrel (*r*, Pl. I, *A*) which had been rendered gas tight by a coat of shellac was used. The gas was collected by displacement of water previously saturated with gas.

OPERATION.

The furnace having been brought to a temperature of 1,070° to 1,080° C. at its center, the retort charged with 400 grams of coal and 100 grams of coke, as shown in figure 1, and the train of by-product

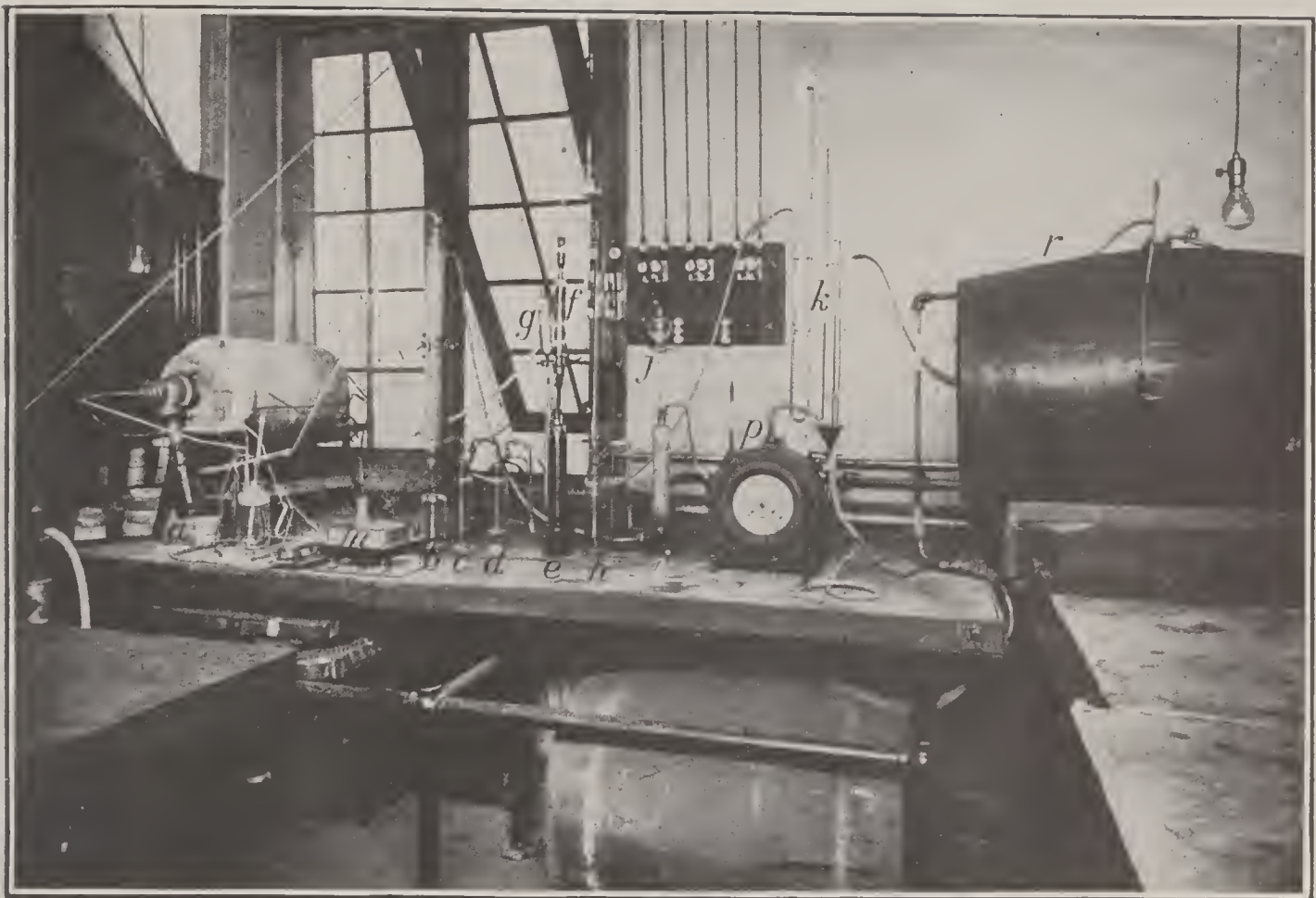
apparatus made ready, the retort was quickly placed in the furnace and the fire-clay doors were replaced. Connection was then made with bottle *a* (see Pl. I, *A*) and temperature readings were taken at intervals of five minutes. The temperature of the furnace is lowered to 720° to 750° by the introduction of the retort, but after about five minutes begins to rise again at the rate of 5° to 6° per minute. Gas begins to be evolved about five minutes after the retort is placed in the furnace. Bottles *a*, *b*, *c*, and *d*, and the tower *e* were weighed with their connections and contents before and after the test. The gain in weight, together with a correction for water evaporated (based on the volume of gas and its temperature), was taken as tar, water, and ammonia. These weighings were made with an accuracy of 0.2 gram (0.05 per cent on the coal sample used). An approximate separation of tar and water was made, but the method was necessarily crude and no claim is made for accuracy nearer than 1 per cent. After all the tar and liquor from bottles *a*, *b*, *c*, and *d* were collected the bulk of the aqueous liquor was decanted and the tar washed thoroughly with a measured quantity of water in six or eight successive portions. The water from tower *e* was used as part of the wash water. These washings were added to the decanted liquor and the whole was measured. The tar was then distilled to 180° C. and the water in the distillate was measured. The total measured amount of water less the wash water added was subtracted from the total tar and water weighed, and the difference was taken as dry tar. For ammonia determination the aqueous liquor and washings were made up to definite volume and aliquot portions were distilled with alkali, the ammonia was received in excess of normal H_2SO_4 and the surplus acid was titrated with normal NaOH and cochineal. The degree of washing necessary to remove all ammonia from the tar was determined by analyzing successive washings, and an excess over this amount was used.

The water in funnel *g* (100 cubic centimeters) and the KOH solution in funnel *j* were admitted to the towers below in small successive portions during the test. The KOH liquor was collected after the test, made up to definite volume and its content of CO_2 determined by evolution with acid and absorption in weighed potash bulbs according to Hillebrand's method.^a A blank was run on the original KOH solution and correction made accordingly.

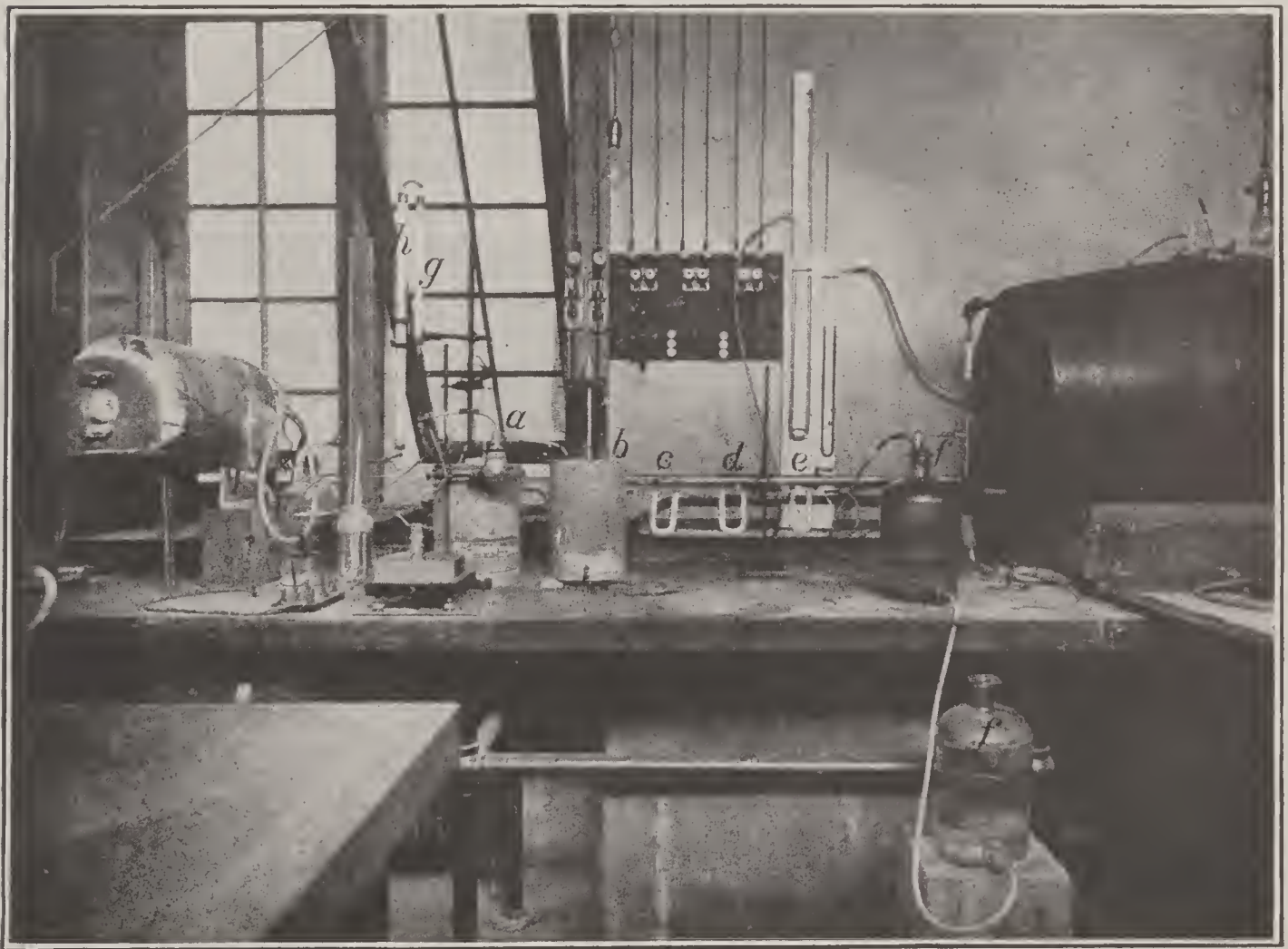
H_2S was determined in the KOH liquor by acidifying a small portion diluted to 400 or 500 cubic centimeters and titrating with decinormal iodine solution.

The gas was measured by the meter, the collecting reservoir being used merely for the purpose of obtaining a true average sample.

^a Hillebrand, W. F., The analysis of silicate and carbonate rocks: Bull. U. S. Geol. Survey No. 305, 1906, p. 150.



A. APPARATUS USED IN DISTILLING 400-GRAM SAMPLES OF COAL IN IRON RETORT.



B. APPARATUS USED IN DISTILLING 10-GRAM SAMPLES OF COAL IN PLATINUM RETORT.

The air in the apparatus (about 0.2 cubic foot) at the beginning of a test was allowed to mix with the gas, and the average analysis was corrected to an air-free basis, all the oxygen present being assumed as due to air. The meter reading, however, represents the true yield of gas, for the same volume remains in the apparatus after the test as before. There is a small error in obtaining the average analysis, as the gas remaining in the apparatus at the close is not of the average composition. Successive samples of gas were taken during the progress of the test, through a T connection between the meter and reservoir.

The coke was removed from the retort and weighed to 0.5 gram. A small amount of tar (less than 0.5 per cent) remains on the walls of the delivery pipe.

By means of the gages (*k*, Pl. I, *A*) a suction of about 2 inches of water was maintained beyond the meter and the gas pressure in bottle *b* was observed. This pressure varied from 8 to 25 inches of water and served incidentally to indicate leaks in the apparatus. The test was continued until gas practically ceased to be evolved—that is, until less than 0.01 cubic foot per minute was produced. The time required to reach this point varied somewhat with the coal but was usually about one hour. The inside temperature (at the surface of the coal) usually attained 800° C. The furnace temperature was not allowed to rise above 1,100° C.

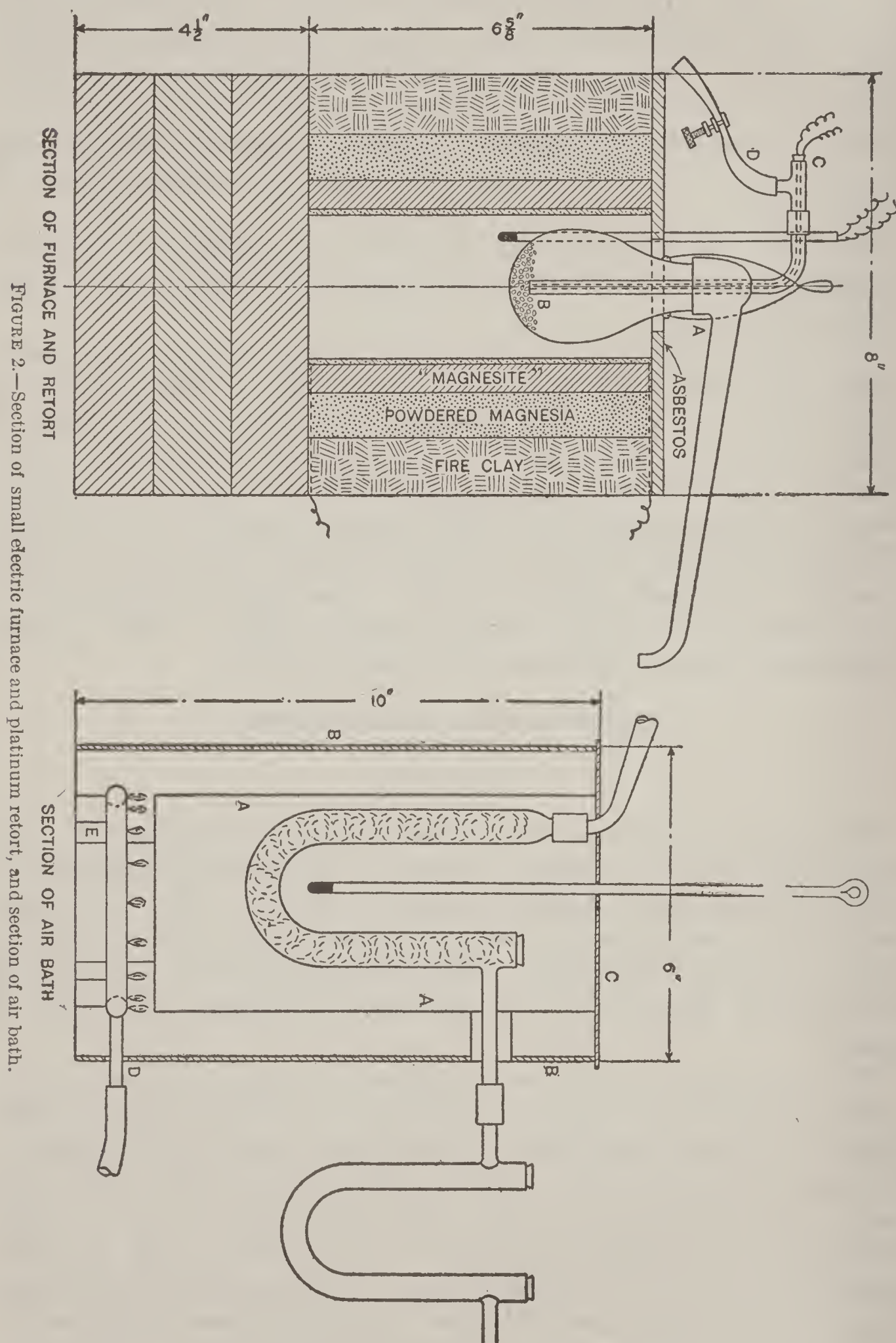
TESTS IN PLATINUM RETORT.

APPARATUS.

For the purpose of comparing coals in respect to the quantity and composition of their volatile products at different temperatures, a small platinum retort having a capacity of about 150 cubic centimeters was used, the retort being provided with a platinum cover, delivery tube, and inlet tube. The arrangement of the apparatus is illustrated in Plate I, *B*, and the detail of furnace and retort in figure 2.

The retort (*a*, Pl. I, *B*) was connected by means of heavy rubber tubing protected by asbestos to a 6-inch U tube and 6-inch straight tube, both tubes being filled with absorbent cotton and inclosed in air baths (*b*) maintained at 110° C. Following the tubes containing cotton were two 5-inch U tubes containing CaCl₂ (*c* and *d*), a protecting tube containing the same (*e*), and finally a pair of 5-liter aspirator bottles (*f*) for collecting gas. The water in the bottles had been previously saturated with gas. One bottle was graduated for measurement of the gas and contained a thermometer. The cotton tubes were previously dried in a current of air at 110° C. Connected to the inlet tube of the retort was a 20-inch straight tube containing

CaCl_2 (*h*) and a 12-inch tube containing soda lime (*g*) for drying and purifying the air or nitrogen entering the retort. Nitrogen for these tests was prepared by drawing a slow current of air first through



alkaline pyrogallol solution in two wash bottles and then over heated copper gauze in a combustion tube. The nitrogen prepared in this way contained from 0.2 to 0.4 per cent of oxygen.

As shown in figure 2, the small vertical electric furnace was similar in construction to the large furnace used in the 1-pound tests, the dimensions differing, however, as indicated. The retort has a ground joint at A, which can be kept gas tight if shaped by a hard-wood form and polished with fine emery cloth before each test. The inner end of the platinum inlet tube is 10 millimeters above the bottom of the retort and the junction of the inside thermocouple (B) 5 millimeters above the bottom. It is important that the position of this thermocouple be kept the same in parallel tests, for a slight difference in its elevation materially affects the temperature reading. The wires of the couple were insulated by fine porcelain tubes, but the junction itself was bare. At C the wires of the thermocouple passed through a cork stopper and a coating of sealing wax; D is the inlet for dry nitrogen or air. The retort was placed in the furnace always at the same height and the temperature of the furnace was taken at the level of the bottom of the retort next the furnace wall.

In figure 2 is shown also the air bath for heating the tubes containing cotton. The inner cylindrical chamber (A) was of tin and was surrounded by a jacket of sheet asbestos (B). The cover (C) was of asbestos. The ring burner (D) encircles the block (E) which supports the bath.

OPERATION.

It was found advisable, on account of the necessity of aspiration in the tar and water determinations, to run the tests for gas separately. For the gas tests, therefore, the platinum retort was connected directly to the gas-collecting bottle, the tar and water being disregarded. The furnace temperature having attained constancy at the desired point, 10 grams of air-dried powdered coal was placed in the retort, the joint was made tight, and the air was displaced by nitrogen, a volume of nitrogen being aspirated equal to three times the capacity of the retort. This amount of aspiration was found to reduce the oxygen to less than 1.0 per cent in the atmosphere of the retort. Connection was then made to the gas-collecting bottle, the retort lowered into the furnace, and the time noted. Temperature readings inside and outside of the retort were taken at one-minute intervals, and when the distillation had proceeded to the point desired the retort was quickly removed and cooled by immersion in water.^a A thorough mixture of the gas and nitrogen was obtained by passing them back and forth three times from the gas-collecting bottle through the retort to the nitrogen reservoir. The gas was measured, its temperature taken, and an average sample analyzed. Although a certain proportion of the nitrogen present is undoubtedly produced by the coal, all analyses were calculated to a nitrogen-free basis to eliminate the effect of dilution with the added nitrogen.

^a In some of these experiments the distillation was carried to an end, that is, until no more gas was evolved; in others it was continued for a limited period fixed either independently of other conditions or, in another series, by the attainment of a certain temperature in the coal. *Because of radiation, the maximum temperature reached in the coal was 75 to 120° C. below that of the furnace.*

In the tar and water determinations the gas was disregarded. After the retort was filled with nitrogen, the drying train was connected and the retort lowered into the furnace, the pinchcock at D (fig. 2) being closed. After having been heated for the desired length of time the retort was removed and cooled as before and 4 liters of dry air was drawn through it. During the aspirating process the platinum delivery tube was warmed with a small flame to drive out all water. The gain in weight of the retort cap and delivery tube was determined and, together with the gain in the cotton tubes, plus a correction for light oils, was taken as tar. The gain in the calcium chloride tubes less the correction for light oils was taken as water. In tests at 900° C. and higher it was necessary to use two cotton tubes in order to retain all the tar, though only one is shown in figure 2. As oils volatile below 110° C. are carried over into the calcium chloride tubes and weighed as water, a correction of 5 per cent of the tar weighed is applied, this being based on the maximum percentage of light oil in coke-oven tar according to Lunge.^a The tar and water separation is therefore approximate only, and no claim is made for greater accuracy in the separation than 1 per cent on the coal.

METHODS OF GAS ANALYSIS.^d

In general, the Hempel methods of gas analysis were used throughout the investigation, although certain modifications were used that increased the accuracy.

CARBON DIOXIDE, OXYGEN, ILLUMINANTS, AND CARBON MONOXIDE.

For the determination of CO₂ a 30 per cent solution of commercial NaOH, for oxygen alkaline pyrogallol solution containing 100 grams pyrogallol and 150 grams NaOH per liter, for illuminants fuming sulphuric acid (20 per cent SO₃), and for CO ammoniacal cuprous chloride solution according to Winkler's formula^b (250 grams NH₄Cl and 200 grams Cu₂Cl₂ in 1 liter, mixed just before use with one-third volume aqua ammonia of specific gravity 0.91) was used. A record of the use of each pipette was kept by noting upon it the volume of gas absorbed during each determination. For the determination of more than 12 per cent of CO three pipettes were used successively.

BENZENE.

For the determination of benzene a large amount of experimental work was done in testing two methods, neither of which proved entirely satisfactory. The method of D. A. Morton,^c using sulphuric acid of specific gravity 1.84, was found to give approximately com-

^a Lunge, G., Coal tar and ammonia, 3d ed., p. 81.

^b Winkler, C., Technische Gas Analyse, 2d German ed., p. 77.

^c Jour. Am. Chem. Soc., vol. 28, 1906, p. 1728.

^d See Addenda, p. 56.

plete absorption of the benzene from benzene and air mixtures in three minutes' shaking; but for coal gas containing various other hydrocarbons as well as benzene the method did not yield concordant results on the same sample and therefore was discarded. The method of L. M. Dennis and E. S. McCarthy,^a using an ammoniacal solution of ammonium nickel cyanide, was not found satisfactory. The absorption proved incomplete from known mixtures of benzene and coal gas in two minutes' treatment carried out as directed by the authors, and concordant results on the same sample could not be obtained.

In giving results of the gas analyses of the present investigation, therefore, no attempt has been made to differentiate the constituents absorbed by fuming sulphuric acid, designated as illuminants.

HYDROGEN.

In most of the tests hydrogen was determined separately by means of palladium asbestos, as recommended by F. C. Phillips,^b the method being that of Winkler.^c Palladium black was precipitated upon acid-washed ignited asbestos by the action of alkaline sodium formate on palladium chloride solution, the product being then washed, dried, and ignited at a moderate red heat. A mixture of the gas residue (after removal of CO) with air, equivalent to an oxygen-hydrogen ratio of at least 2:1 by volume, was passed slowly over the palladium in a small U tube maintained at 50° to 70° C. by a water bath. After this mixture was passed three times through the tube the contraction was complete and the gas was cooled by passing once through the tube immersed in water at room temperature. A water-jacketed burette was used for this determination, and a Hempel pipette containing distilled water was used for receiving the gas after passage through the palladium tube. The palladium asbestos must be dried thoroughly after each combustion of hydrogen and must be carefully protected from contamination with acid fumes. According to Phillips hydrogen is completely burned under these conditions and hydrocarbons are not affected. The writers have verified this statement by tests with pure electrolytic hydrogen and also with samples of natural gas, testing for the formation of CO₂.

METHANE AND ITS HOMOLOGUES.

For the determination of paraffin hydrocarbons of the general formula C_nH_{2n+2} (methane, ethane, etc.), Winkler's method of slow combustion by a heated platinum spiral,^d as modified by L. M. Dennis and C. G. Hopkins,^e was used.

^a Jour. Am. Chem. Soc., vol. 30, 1908, p. 233.

^b Am. Chem. Jour., vol. 16, 1893, pp. 164-168.

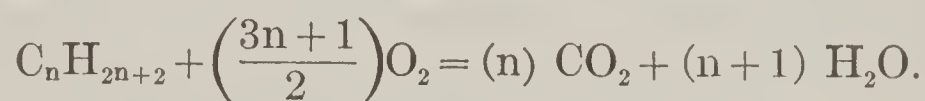
^c Winkler, C., Technische Gas Analyse, 2d German ed., pp. 145-150.

^d Idem, pp. 155-157.

^e Hempel, W., Gas analysis (trans. of 3d German ed.), p. 138.

The combustion pipette was of glass. The spiral was made of about 10 inches of No. 24 platinum wire and the ends of the spiral were welded to somewhat larger platinum wires which, insulated by glass tubes, passed downward through the rubber stopper and were connected to the source of the electric current. It was found necessary to avoid the use of any baser metal than platinum in the fittings of the pipette, as a considerable error is introduced thus by oxidation of the metal.

The total contraction and CO_2 produced by the combustion having been determined, and the contraction due to hydrogen separately determined by palladium and subtracted, the result indicated the contraction and the CO_2 due to the burning of methane and its homologues. As shown by E. H. Earnshaw,^a the total volume of hydrocarbons of the type $\text{C}_n\text{H}_{2n+2}$ and also the value of n could then be calculated, showing the average composition of the hydrocarbon mixture. For a given amount of contraction and CO_2 the total volume of $\text{C}_n\text{H}_{2n+2}$ is the same, regardless of the relative percentages of CH_4 , C_2H_6 , C_3H_8 , etc. Thus:



If V = volume of $\text{C}_n\text{H}_{2n+2}$

$$(1) \text{ Contraction} = \left(V + \frac{3n+1}{2} V\right) - nV = V\left(\frac{n+3}{2}\right)$$

$$(2) \quad \text{CO}_2 = Vn.$$

$$\text{By combining (1) and (2) } V = \frac{2 \text{ contraction} - \text{CO}_2}{3}$$

and

$$n = \frac{\text{CO}_2}{V}$$

Without further data it is impossible to determine the relative percentage of any one of the hydrocarbons when more than two are present.

If we assume, however, that only methane (CH_4) and ethane (C_2H_6) are present, and find, for example, 1.25 for the value of n and 24 per cent for the total $\text{C}_n\text{H}_{2n+2}$, then ethane is 25 per cent of the total, or 6 per cent; if n is found to be 1.33 and the total 24 per cent, then ethane is 8 per cent.

^a Jour. Franklin Inst., September, 1898.

NOTE.—The method of determining methane and hydrogen in gas mixtures by burning or exploding with air or oxygen, and not separately determining the hydrogen, introduces a serious error when ethane or higher hydrocarbons are present. This method, under the last-mentioned conditions, indicates a percentage of hydrocarbons that is greater and a percentage of hydrogen that is less than the true percentage.

SUMMARY AND INTERPRETATION OF RESULTS.

COALS TESTED.

The following tables show the source and composition of the coals used for the tests herein described:

TABLE 3.—Source of coal samples used in tests.

Laboratory No. ^a	State.	Post-office.	Seam or bed.	Mine.	Date collected.
1	Illinois.....	Zeigler, Franklin County..	No. 7.....	Zeigler.....	June 23, 1907
3	Pennsylvania.....	Connellsville, Fayette County.	Pittsburg.....	Leisenring No. 1.	June 20, 1907
10	West Virginia.....	Page, Fayette County.....	No. 2 gas.....	Ansted.....	Oct. 7, 1907
11	Wyoming.....	Dietz, Sheridan County ^b	No. 1.....	Sept. 24, 1907
16	Virginia.....	Pocahontas, Tazewell County.	No. 3.....	Baby.....	Nov. 23, 1907
18	Wyoming.....	Diamondville, Uinta County.	No. 1.....	Dec. 9, 1907
23	Illinois.....	Harrisburg, Saline County	No. 5.....	No. 8.....	Jan. 30, 1908
25	Utah.....	Castle Gate, Carbon County	Mar., 1908
46	Wyoming.....	Near Kemmerer, Uinta County.	Willow Creek.....	Mar., 1909

^a Special laboratory number not corresponding to those of the general laboratory of the fuel-testing plant.
^b Subbituminous.

TABLE 4.—Analyses of coals tested.

Laboratory No.....	1.	3.	10.	11.	16.	18.	23.	25.	46.
<i>Bulk sample (100 pounds).</i>									
Air-drying loss.....	1.63	0.10	0.69	14.63	0.81	2.30	5.21	0.56	1.64
Analysis of air-dried sample:									
Moisture ^a	{ 7.67	1.10	.87	11.45	.35	2.64	1.96	2.30	2.17
	7.40	1.09	.98	10.83	.59	3.48
Volatile matter.....	30.38	30.67	32.46	^b 35.74	20.93	42.23	32.05	40.24	34.01
Fixed carbon.....	54.32	60.35	61.66	47.74	75.51	50.65	56.75	51.38	58.37
Ash.....	7.63	7.88	5.01	5.07	3.21	4.48	9.24	6.08	5.45
Computed to "as received" basis:									
Moisture ^a	9.19	1.18	1.55	{ 24.40	} 1.16	4.88	7.07	2.85	3.74
				21.96					
Volatile matter.....	29.89	30.64	32.22	30.52	20.76	41.25	30.37	40.04	33.46
Fixed carbon.....	53.41	60.31	61.26	40.75	74.90	49.49	53.80	51.06	57.44
Ash.....	7.51	7.87	4.97	4.33	3.18	4.38	8.76	6.05	5.36
Sulphur.....38	.61	.41	1.48	.42	.91
Nitrogen.....	1.15	1.07	.97	1.27	1.16
<i>1-pound mine sample corresponding to above.</i>									
Can No.....	3,249	3,245	3,625	(c)
Analysis on basis of sample as received:									
Moisture.....	11.82	3.24	2.65	12.28
Volatile matter.....	27.66	27.13	29.69	36.96
Fixed carbon.....	55.10	62.52	63.50	45.88
Ash.....	5.42	7.11	4.16	4.88
Sulphur.....	.46	.95	1.29	.45
Carbon.....	67.87	78.00	60.44
Hydrogen.....	5.44	5.24	5.36
Nitrogen.....	1.34	1.23	1.32
Oxygen.....	19.47	7.47	27.55
Calories.....	6,645	7,733	8,104	5,774
British thermal units.....	11,961	13,919	14,587	10,393

^a Second determinations given were made on same samples twelve to eighteen months later.
^b Determined by modified method; Somermeier, E. E., Jour. Am. Chem. Soc., vol. 28, 1906, p. 1002.
^c Air-dried No. 11, same as above.

TESTS OF COAL IN IRON RETORT FOR BY-PRODUCTS OF COKING.

SUMMARIES OF TESTS.

In order to determine the adaptability of certain western coals to the production of gas, tar, and ammonia as by-products of coke making or of gas manufacture, one southern Illinois coal, two Wyoming coals, and one Utah coal were tested in the iron retort; and for standards of comparison several tests were made on the well-known Connellsville and Pocahontas coals of the Appalachian region. A few experiments also were carried out with the Connellsville coal for the study of the effect of moisture in the coal on the ammonia yield. Tables 5, 6, and 7 give summaries of the average results. Detailed data of the individual tests will be found on pages 45 to 47.

TABLE 5.—Results of by-product tests.

[See p. 25 for analyses and description of coals.]

Laboratory No	16.	3.	23.	11.	11 (air dried).	25.	46.
Number of tests averaged	2	6	2	4	2	2	2
Coke per cent.	79.1	71.4	63.1	44.7	53.0	58.6	63.9
Tar do.	7.2	11.3	11.9	7.1	5.5	12.3	10.3
Water do.	1.3	4.9	10.7	27.5	19.0	11.8	10.0
Ammonia pounds of sulphate per ton.	12.9	23.8	25.3	27.2	26.7	26.3	26.3
CO ₂ per cent.	.44	.72	1.20	8.14	8.41	3.13	2.13
H ₂ S do.	.07	.25	.46	.08	.11	.24	.30
Gas cubic feet per ton ^a .	9,700	8,140	8,400	7,830	8,170	7,620	7,940
Composition of gas: ^b							
Illuminants	1.4	3.2	3.0	2.2	2.6	5.7	5.5
CO	3.2	5.1	7.4	19.5	21.4	14.9	12.3
CH ₄ , C ₂ H ₆ , etc.	26.4	27.8	^c 26.3	18.1	^c 22.6	27.2	25.4
H	67.8	61.0	^c 56.8	54.0	^c 49.3	47.8	53.1
N	1.2	2.9	6.5	6.2	4.1	4.4	3.7
Value of n in C _n H _{2n+2}	(c)	1.27	(c)	1.18	(c)	1.32	1.29
Total volatile products (without moisture)	19.7	27.4	29.8	33.3	35.5	38.5	32.4
Water of constitution1	3.7	3.6	5.5	7.5	8.9	6.3
Inert volatile matter ^d7	4.7	5.1	14.0	16.3	12.4	8.8

^a Calculated to dry basis at 0° C. and 760 millimeters pressure, free of air and CO₂.
^b Calculated to CO₂ and O free basis.
^c Hydrogen not determined separately by palladium but calculated from combustion; CH₄ probably high and H low.
^d Sum of CO₂, ammonia, and water of constitution.

The conditions in all the above tests were approximately those described under "Methods" (pp. 15-19).
The western coals give larger ammonia yields under the laboratory conditions than the Connellsville coal. The bituminous coals, No. 25 (Utah) and No. 46 (Wyoming), yield a gas of good quality, nearly twice as high in percentage of illuminants as that from the Connellsville coal. The yield is somewhat smaller than the Connellsville yield, however, when the gas is freed of CO₂. Coal No. 23, from Harrisburg, Ill., gives a somewhat higher yield of gas than the Connellsville coal and the gas is of similar composition. All these coals, except No. 11, produce coke in the laboratory test, but this result can not be relied on even as an indication of industrial coking possibilities.

The subbituminous Wyoming coal, No. 11, yields large quantities of gas very high in CO_2 and CO . Comparative tests on this coal as received and air-dried are shown in the above table. In order to be fairly comparable, however, they must be computed to an equivalent basis, that of the moisture-free material, and the results expressed in percentages of dry coal, as follows:

TABLE 6.—*Tests of coal from Sheridan field, Wyoming (laboratory No. 11), computed to dry basis.*

	Coal distilled as received.	Coal distilled in air-dried state.
Coke.....per cent..	57.3	59.9
Tar.....do.....	9.1	6.2
Water.....do.....	35.3	21.5
Ammonia.....pounds sulphate per ton..	35.0	30.2
CO_2per cent..	10.4	9.6
Gas at 0° C. and 760 mm. pressure, free of CO_2 and air, and dry ...cubic feet per ton..	10,020	9,250
Water of constitution.....per cent..	7.1	8.5
Inert volatile matter.....do.....	18.0	18.4

The results as thus expressed show that the absolute quantities of products to be obtained from the coal, either as mined or partly dried, amount to the above-stated percentages of the dry material present. The ammonia yield on the basis of dry material is greater from the moist coal than from the air-dried coal; on the same basis also the CO_2 and CO are slightly greater from the moist coal, but not so much greater as to lead to the conclusion that any considerable amount of the large CO_2 and CO production is to be ascribed to the action of water vapor on carbon.

EFFECT OF MOISTURE IN COAL ON AMMONIA YIELD.

In order to test further the influence of moisture on ammonia yield a few tests were run on Connellsville coal moistened so as to contain 9.6 per cent of water, and on the coal as received, with 1.2 per cent of water, under conditions otherwise as nearly the same as possible.

TABLE 7.—Comparative by-product tests of dry and wet coal.

[Coal No. 3, with 1.2 and 9.6 per cent of moisture.]

	Percentages of coal as used.		Percentages of moisture-free coal.	
	Distilled dry.	Distilled wet.	Distilled dry.	Distilled wet.
Number of tests averaged.....	2	2	2	2
Coke.....per cent..	71.4	66.6	72.3	73.7
Tar.....do...	10.2	9.2	10.3	10.2
Water.....do...	5.9	13.3	6.0	14.7
Ammonia.....pounds of sulphate per ton..	25.0	24.3	25.3	26.9
Gas at 0° C. and 760 millimeters pressure, dry..cubic feet per ton..	7,900	6,640	8,000	7,350
Composition of gas:				
CO ₂	1.8	1.8		
Illuminants.....	2.7	2.8		
CO.....	5.0	5.1		
CH ₄ , C ₂ H ₆ , etc.....	29.1	33.3		
H.....	58.7	55.0		
N.....	2.7	2.0		
Value of n in C _n H _{2n+2}	1.28	1.17		

On the basis of dry material, the ammonia yield seems to be greater again with the wet coal. The gas yield is lower with the wet coal, but in composition the gas is somewhat richer in hydrocarbons.

VARIATION IN GAS COMPOSITION DURING TEST.

The analyses of gas samples taken successively during the progress of the 400-gram by-product tests show the familiar increase of hydrogen and decrease of hydrocarbons as the carbonization proceeds. The detailed analyses are given on pages 46 to 47. It is of interest to note that samples taken early in the test (after the lapse of 20 to 25 per cent of the coking time) contain in the high-grade coals 50 to 55 per cent of methane and its homologues and that the proportion of ethane and higher homologues is considerably greater in the early samples. The early sample from Pocahontas coal is not only rich in hydrocarbons but contains also a large percentage of hydrogen (40 to 45 per cent), wherein it differs from the other coal types.

INERT VOLATILE MATTER.

In the tabulated results (Table 5, p. 26) are given percentages of inert volatile matter based on the experimental measurement of water of constitution, CO₂, and ammonia. It will be seen that this inert material varies from 4 per cent of the total volatile in Pocahontas coal to 42 per cent in the subbituminous coal of the Sheridan field, Wyoming. The results of tests on 10-gram samples of coal given on pages 38-40 and 49-54 are similar to those above noted. These values obtained experimentally are somewhat smaller than those obtained by calculation, where all of the oxygen is assumed to combine with hydrogen, forming water.

S. W. Parr^a proposes a method for the determination of available hydrogen in coal by the use of curves which show the relation of available hydrogen to volatile carbon and total carbon. These curves are platted from the data of ultimate analyses, fixed points being established, and from available hydrogen values which were calculated by converting all of the oxygen to water. The sum of available hydrogen, volatile carbon, and sulphur is taken as combustible volatile and the difference between this and the total volatile as inert volatile. Many of the values thus deduced for the inert volatile matter are higher than those obtained in the present investigation by experimental measurement for the reason that in obtaining them the presence of CO₂ and CO in the volatile products was not considered; but the experimental results of the present investigation uphold the contention of Parr and others that considerable proportions of inert noncombustible materials are contained in the volatile products of coal and that this factor varies with the type of coal.

TESTS OF COAL IN PLATINUM RETORT.

TOTAL GAS AT VARIOUS TEMPERATURES.

In order to compare different coals in the amount and composition of their total gaseous products at medium and high temperatures, a series of tests was run in the platinum retort on 10 grams of coal, placed in the furnace at certain fixed temperatures and heated until gas practically ceased to be evolved. These tests were run in an atmosphere of nitrogen; the CO₂ and CO found are therefore products of destructive distillation, not of combustion. The gas analyses as given have been calculated to a nitrogen and oxygen free basis, it being assumed that any oxygen present is due to air admitted accidentally during the mixing and transferring of the gas sample. The volumes given under "gas yield" have also been corrected for air in a few instances where oxygen was shown by the analysis. No determinations of tar and water were made in these tests. Analyses of the different coals are found on page 25.

TABLE 8.—Total gas yield and composition at different temperatures.^b
[From 10 grams air-dried coal.]

	Coal No. 1 (Zelgler, Ill.).						
Temperature of furnace.....° C..	500.	600.	700.	800.	900.	1,000.	1,100.
Highest temperature reached in coal.....° C..	390	480	585	685	811	920	1,026
Gas at 25° C.....cubic centimeters..	197	535	980	1,550	2,335	2,700	3,120
Composition of gas:							
CO ₂	23.8	7.6	6.4	3.9	2.5	2.7	1.8
Illuminants.....	6.5	5.0	4.1	3.3	3.2	3.7	4.0
CO.....	16.5	16.1	21.1	16.9	15.2	15.1	16.1
CH ₄ , C ₂ H ₆ , etc.....	49.5	55.0	41.5	34.4	27.8	23.1	19.4
H.....	3.7	16.3	26.9	41.5	51.3	55.4	58.7
Value of n in C _n H _{2n+2}	1.42	1.29	1.21	1.16	1.22	1.18	1.23

^a Jour. Am. Chem. Soc., vol. 29, 1907, p. 585; Bull. Illinois State Geol. Survey, No. 3, 1906.
^b Data given are averages of results of individual tests to be found elsewhere in this paper.

TABLE 8.—*Total gas yield and composition at different temperatures—Continued.*

	Coal No. 3 (Connellsville, Pa.).						
Temperature of furnace.....° C..	500.	600.	700.	800.	900.	1,000.	1,100.
Highest temperature reached in coal.....° C..	390	474	589	705	812	922	1,010
Gas at 25° C.....cubic centimeters..	161	718	1,220	1,723	2,080	2,900	3,530
Composition of gas:							
CO ₂	15.9	4.2	3.2	2.0	1.1	1.2	1.0
Illuminants.....	9.1	7.1	4.3	4.5	4.8	4.6	5.2
CO.....	7.8	6.0	6.3	7.2	7.4	6.4	7.3
CH ₄ , C ₂ H ₆ , etc.....	63.3	64.4	55.8	47.0	33.2	29.0	26.3
H.....	3.9	18.3	30.4	39.3	53.5	58.8	60.2
Value of n in C _n H _{2n+2}	1.69	1.37	1.27	1.21	1.22	1.11	1.15

	Coal No. 16 (Pocahontas).			Coal No. 11 (Dietz, Wyo.).		
Temperature of furnace.....° C..	500.	700.	1,000.	500.	700.	1,000.
Highest temperature reached in coal.....° C..	615	920	600	920
Gas at 25° C.....cubic centimeters..	238	1,185	3,230	517	1,300	3,650
Composition of gas:						
CO ₂	5.5	1.4	.4	54.3	21.7	10.4
Illuminants.....	5.2	3.5	3.7	3.7	3.5	4.5
CO.....	3.5	5.1	4.6	19.6	21.5	22.3
CH ₄ , C ₂ H ₆ , etc.....	70.6	55.2	26.8	18.9	29.4	16.3
H.....	15.2	34.8	64.5	3.5	23.9	46.5
Value of n in C _n H _{2n+2}	1.46	1.19	1.13	1.55	1.19	1.25

TABLE 9.—*Yield of different gaseous products at 500°, 700°, and 1,000° C.*

[Cubic centimeters from 10 grams of coal.]

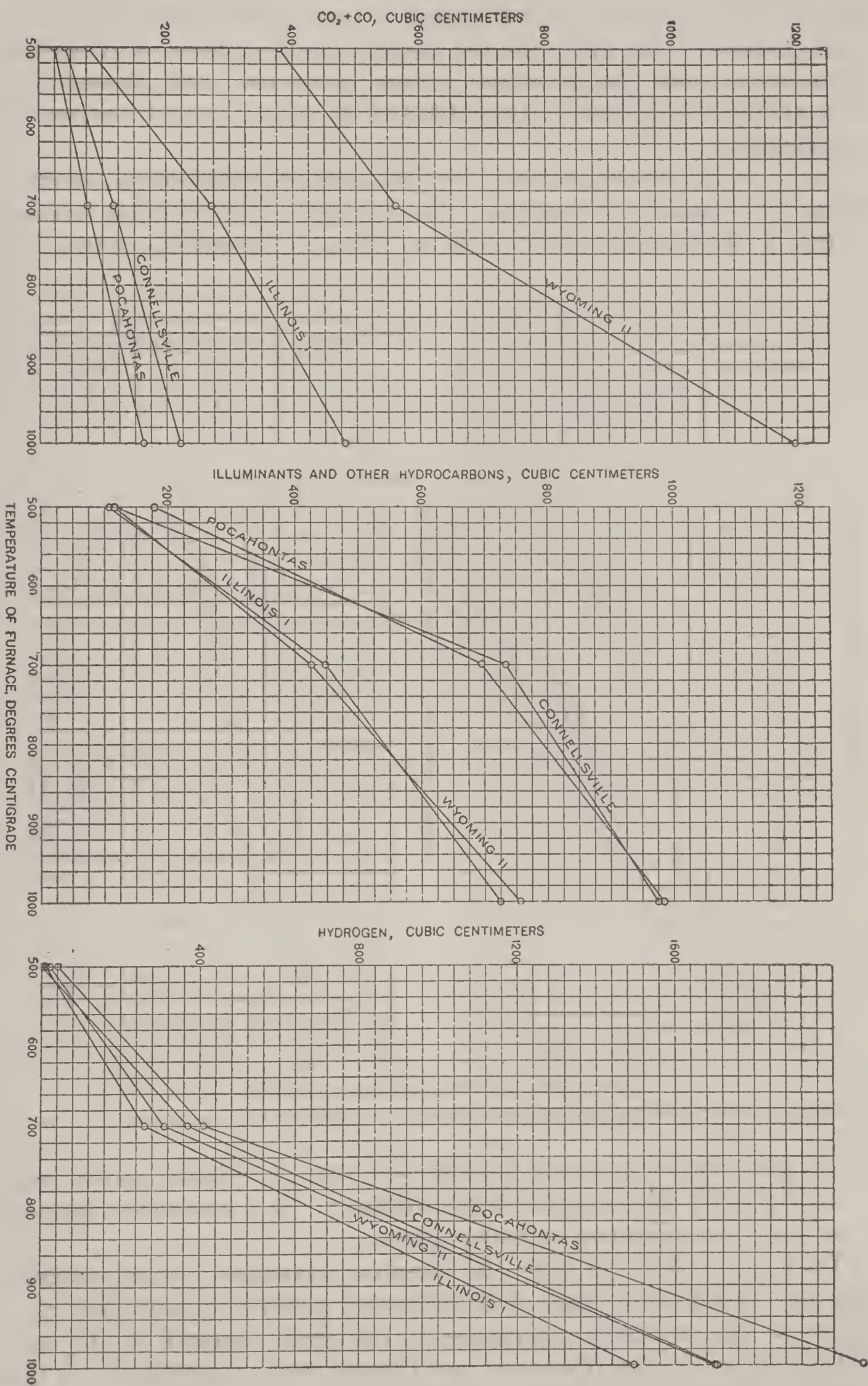
Temperature of furnace.....° C..	500.				700.				1,000.			
No. of coal.....	16.	3.	1.	11.	16.	3.	1.	11.	16.	3.	1.	11.
Total gas.....	238	161	197	517	1,185	1,220	980	1,300	3,230	2,900	2,700	3,650
CO ₂	13	26	47	281	17	39	63	282	13	35	73	380
Illuminants.....	12	15	13	19	42	52	40	46	120	133	100	164
CO.....	8	13	33	101	60	77	207	280	149	186	408	814
CH ₄ , C ₂ H ₆ , etc.....	168	102	97	98	654	681	407	382	866	841	624	595
H.....	37	5	7	18	412	371	263	310	2,082	1,705	1,495	1,697
Value of n in C _n H _{2n+2}	1.46	1.69	1.42	1.55	1.19	1.27	1.21	1.19	1.13	1.11	1.18	1.25

The coals used in the tests above reported were selected as being representative of more or less well defined types and localities.

No. 1 is from the Zeigler mine, in the so-called No. 7 seam of Illinois. It is representative of the noncoking Interior Province coals, among which it ranks high in heating value and steaming qualities. It has high volatile matter and gives trouble by the formation of mine gas.

No. 3 is the well-known coking coal of Connellsville, Pa., of higher heating value and slightly lower volatile matter than No. 1. It is fairly representative of the high-grade steaming and coking coals of the Pittsburgh district. This type is commonly burned with large smoke production in boiler plants.

FIGURE 3.—Total quantities of different gases from 10 grams of air-dried coal at different temperatures.



No. 16 is the well-known Pocahontas coal, representative of the high-grade, low-volatile, "smokeless" coals of the lower West Virginia region. This type has the highest heating value of American bituminous coals, has excellent coking properties, and, though low in volatile matter, gives a large quantity of "thin" gas on destructive distillation.

No. 11 is the subbituminous, low-grade coal of the Sheridan district, Wyoming, commonly known as "black lignite." It is of low heating value, high oxygen content, and no coking properties; contains 20

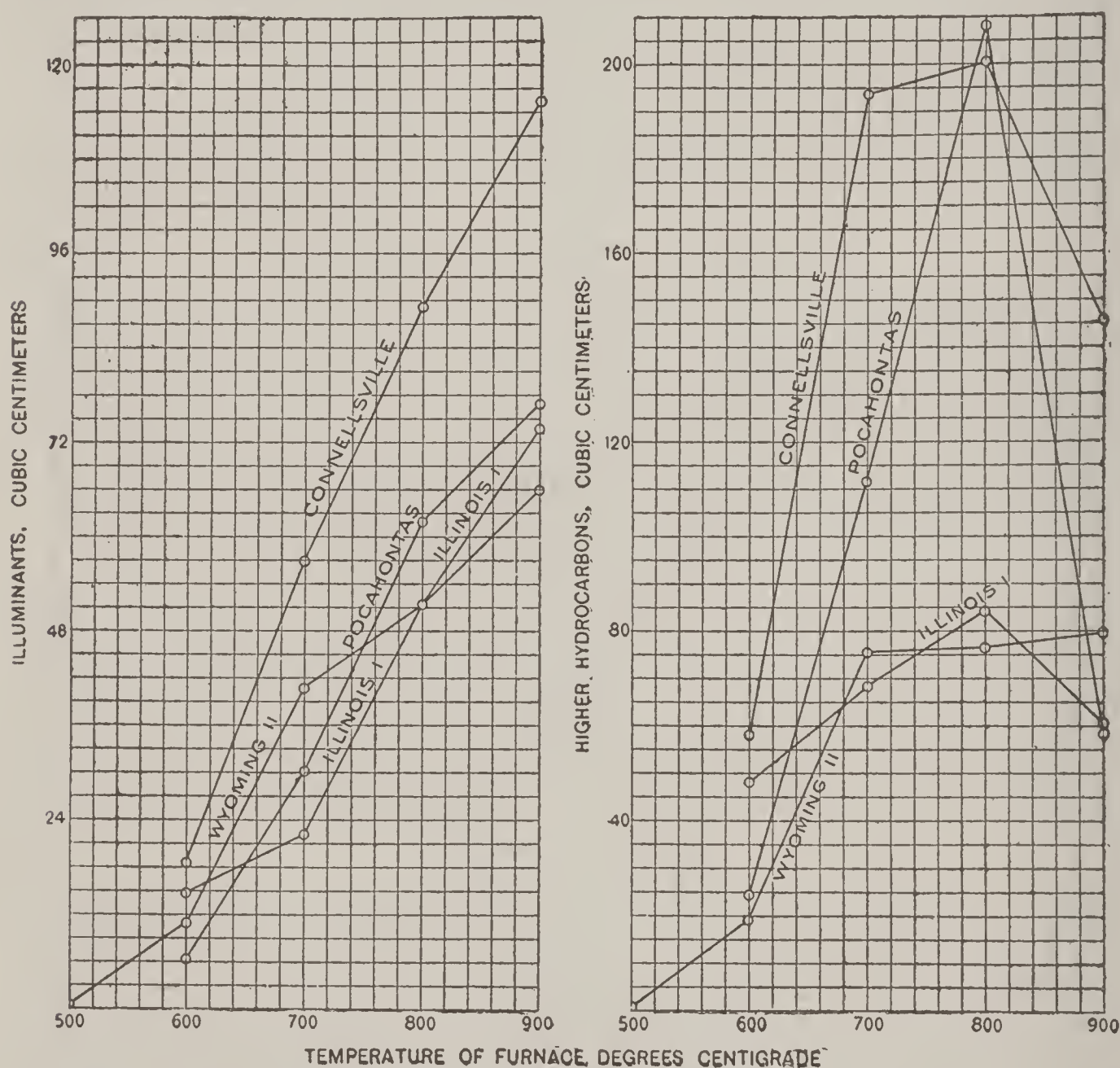


FIGURE 4.—Smoky constituents of early volatile matter; 10 grams of air-dried coal heated ten minutes.

to 24 per cent of moisture and 30 per cent of volatile matter and crumbles badly on exposure to the weather. It is commonly burned with very low efficiency in boiler plants.

Table 9 and figure 3 show the absolute quantities (cubic centimeters per 10 grams of coal) of the different gaseous constituents produced at the several temperatures. The great amount of CO_2 and CO produced by the Wyoming and Illinois coals as compared to the yield of the eastern coals is very noticeable. The eastern coals, on the other hand, produce considerably greater amounts of hydrocar-

bons and hydrogen even at the low and medium temperatures. Hydrogen is given off more abundantly by the Pocahontas coal than by the others, at both low and high temperatures. As shown by the value of n in the saturated hydrocarbons C_nH_{2n+2} , the proportion of higher members of this hydrocarbon series is greater at low temperatures than at high, and greater in the Connellsville type than in the others. In some tests less than half of these hydrocarbons is methane, the remainder being ethane and higher homologues.

VOLATILE MATTER DURING EARLY PERIOD OF HEATING AT VARIOUS TEMPERATURES.

The character of the volatile matter produced during the early stages of heating has more direct bearing on economy in the utilization of fuel, on smoke production, and on the efficiency of furnaces than that of the volatile matter produced at later stages in the heating. It seems probable that in the first products driven off is involved the chief difficulty in obtaining complete combustion. Accordingly, a series of experiments was undertaken to show comparatively the amount and character of the volatile products which different coals evolve during the first brief period of heating at various temperatures. In one series of experiments the period of heating was fixed by the time element alone, ten minutes being adopted as the period best suited to the amount of coal and method of heating. In another series the rise of temperature in the interior of the coal itself was allowed to fix the period, the heating being stopped as soon as the inside temperature reached a point 200° below that of the furnace. By the latter method the period is, at the different temperatures,

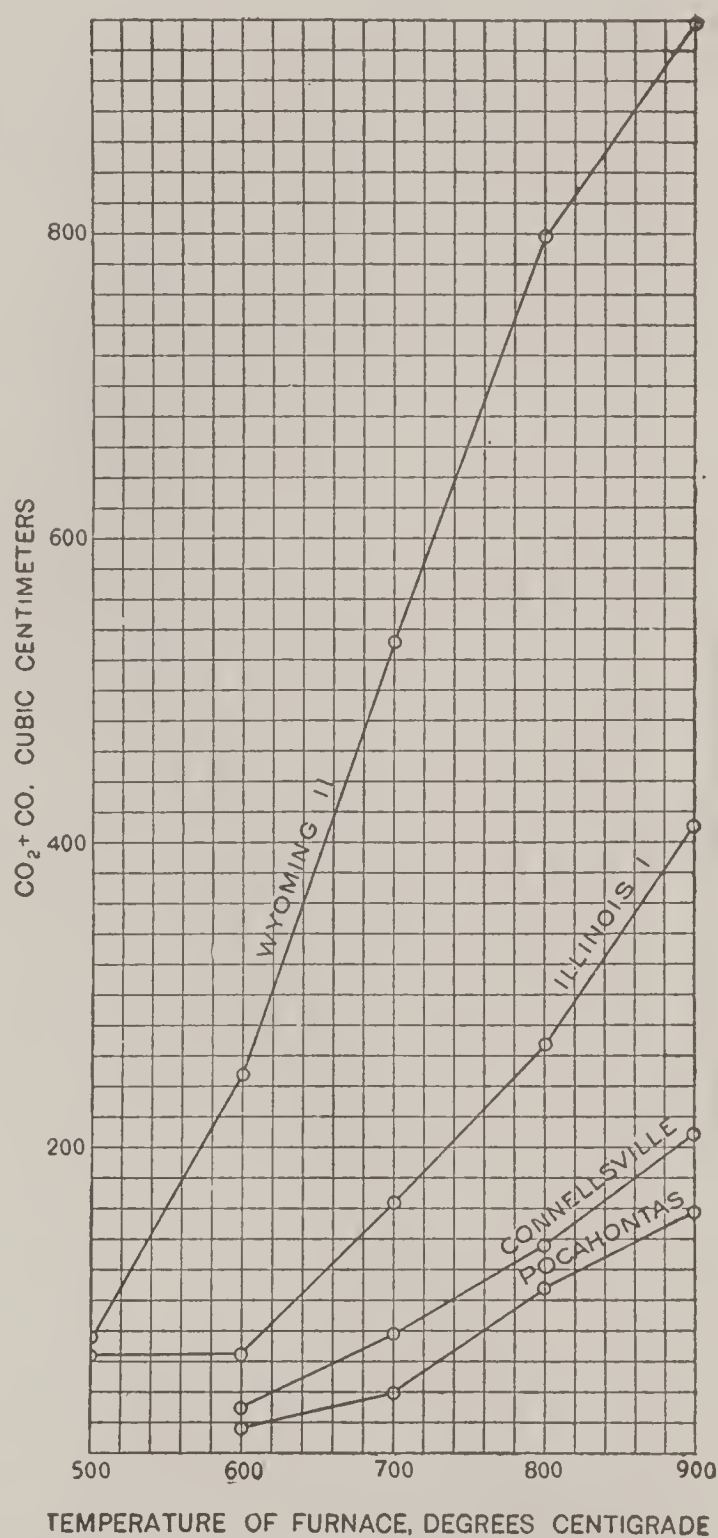


FIGURE 5.—Oxides of carbon in early volatile matter; 10 grams of air-dried coal heated ten minutes.

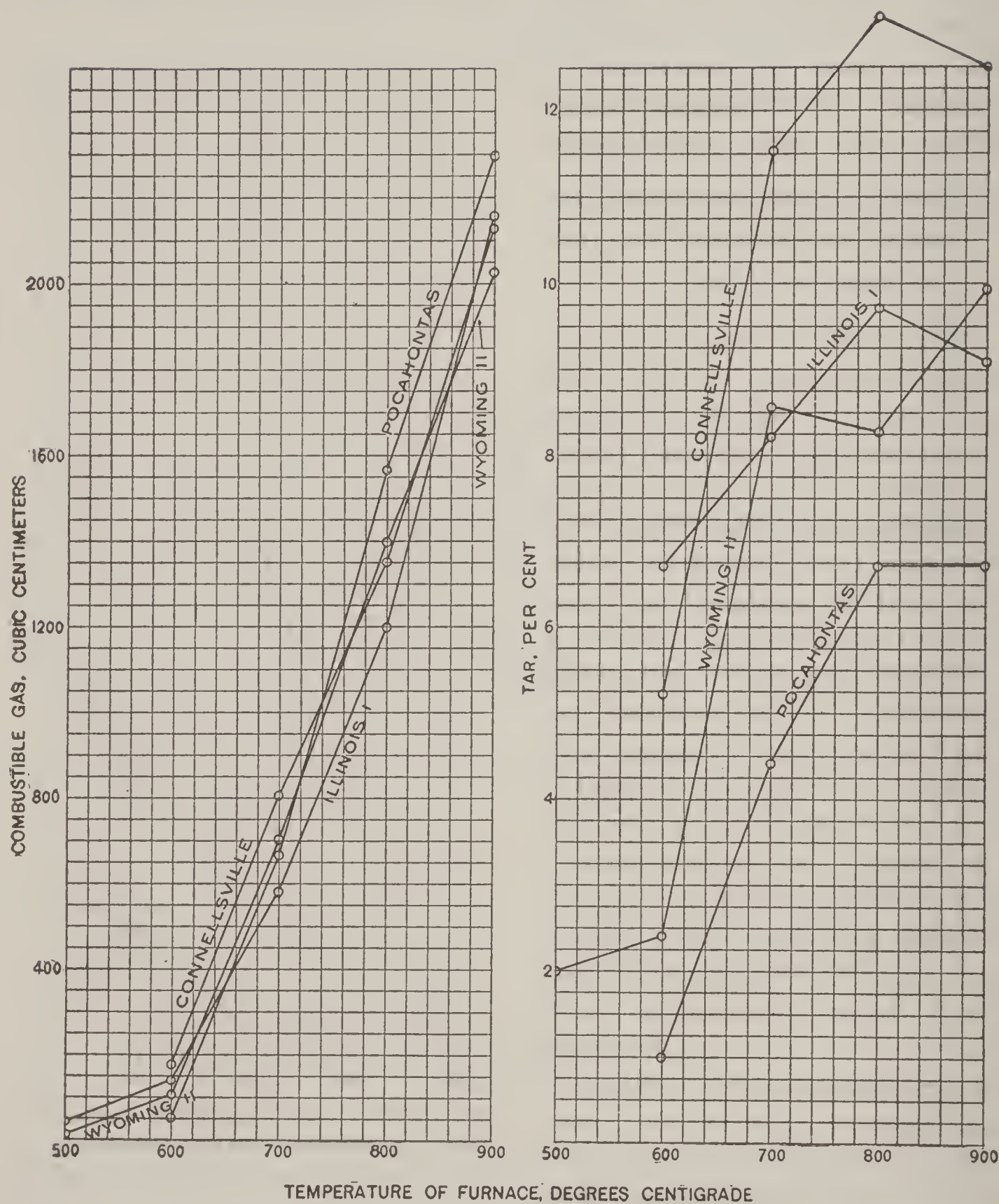


FIGURE 6.—Combustible gases and tar in early volatile matter; 10 grams of air-dried coal heated ten minutes.

more nearly in uniform relation to the total time of evolution of volatile matter.

The coals used for the determination of total gas yield were used also in these experiments; and for the second series two others were added, No. 10, a high-volatile West Virginia gas coal, and No. 18, a high-volatile "long flame" bituminous coal from Diamondville, Wyo. The latter does not coke but is valued locally as a high-grade steam-

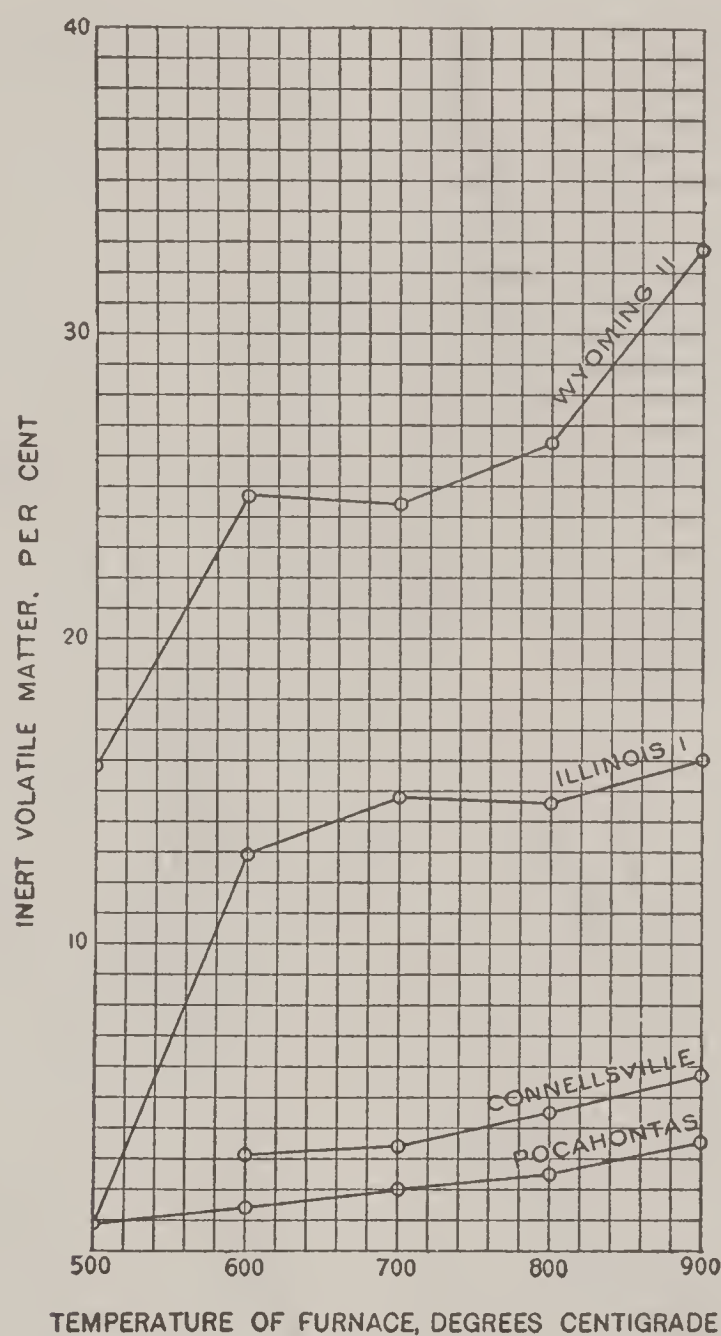


FIGURE 7.—Inert or noncombustible constituents (including moisture) of early volatile matter; 10 grams of air-dried coal heated ten minutes.

ing coal and is particularly well adapted to reverberatory furnaces in smelters, as it gives a long, hot flame. Determinations were made also of tar and water in this early volatile matter.

TABULATED RESULTS, EARLY VOLATILE MATTER.

The results, as compiled from the detailed data given later in the paper, are stated in Tables 10 to 13. The relation of the composition and volume of the volatile matter to the temperature in the two series of experiments is shown graphically in figures 4 to 9.

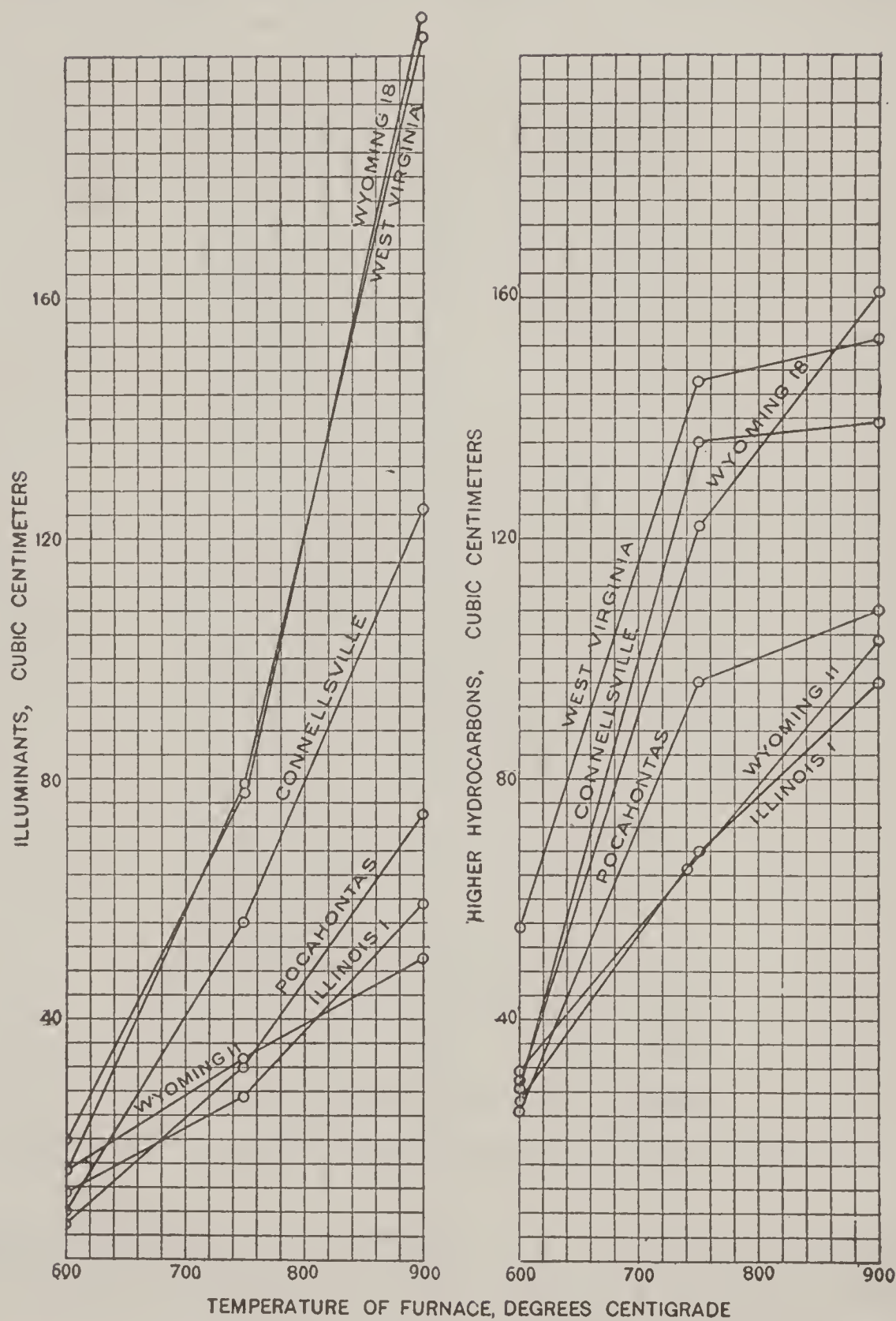


FIGURE 8.—Smoky constituents of early volatile matter; 10 grams of air-dried coal heated to definite temperature.

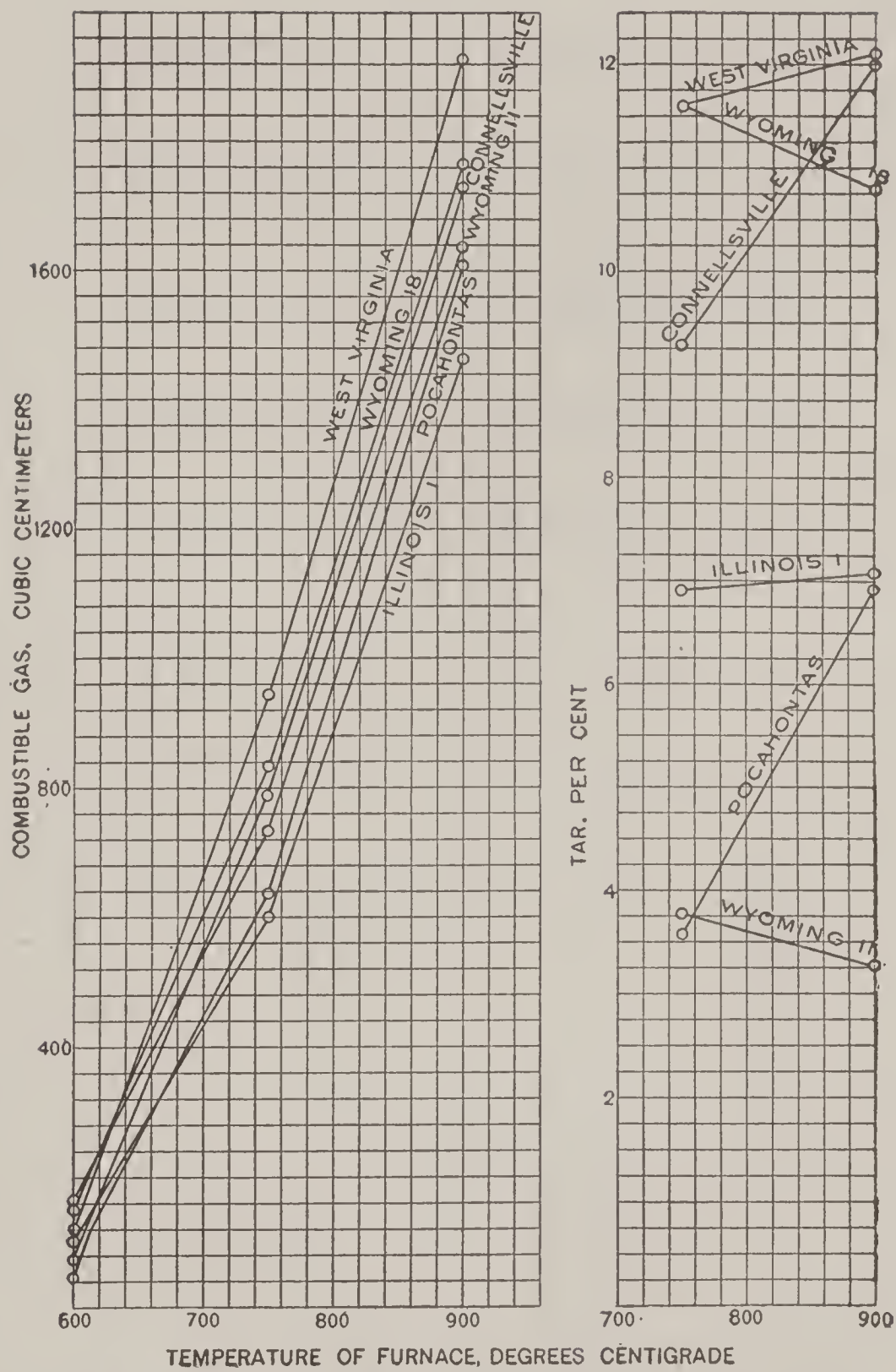


FIGURE 9.—Combustible gases and tar in early volatile matter; 10 grams of air-dried coal heated to definite temperature.

TABLE 10.—Volatile matter in ten minutes' heating of 10 grams of air-dried coal.

	Coal No. 1 (Zeigler, Ill.).					Coal No. 3 (Connellsville, Pa.).				
	500.	600.	700.	800.	900.	500.	600.	700.	800.	900.
Temperature of furnace.....° C.										
Highest temperature reached in coal.....° C.										
Tar.....per cent.	345	440	545	680	9.1	335	441	562	687
Water.....do.	6.7	8.2	9.7	14.4	5.2	11.6	13.2	12.5
Gas at 25° C.....cubic centimeters.	12.2	13.6	13.5	14.4	2.9	2.9	4.0	4.7
Composition of gas: <i>a</i>	90	173	640	1,252	2,240	8	190	829	1,375	2,180
CO ₂	52.7	19.4	9.4	4.3	3.7	7.5	2.8	1.7	2.4
Illuminants.....	0	8.6	3.5	4.1	3.3	10.0	6.9	6.5	5.3
CO.....	18.9	18.0	16.4	17.0	14.6	7.2	6.6	8.2	7.1
CH ₄ , C ₂ H ₆ , etc.....	28.4	50.8	46.2	37.3	30.1	72.7	58.4	44.0	35.3
H.....	0	3.2	24.5	37.3	48.3	2.6	25.3	39.6	49.9
Value of n in C _n H _{2n+2}	1.55	1.23	1.18	1.09	1.42	1.40	1.33	1.19

	Coal No. 16 (Pocahontas).					Coal No. 11 (Dietz, Wyo.).				
	500.	600.	700.	800.	900.	500.	600.	700.	800.	900.
Temperature of furnace.....° C.										
Highest temperature reached in coal.....° C.										
Tar.....per cent.	0.3	1.0	4.4	6.7	6.7	2.4	580	8.3	9.9
Water.....do.	.8	1.2	1.7	2.1	2.7	21.0	18.1	18.7	24.3
Gas at 25° C.....cubic centimeters.	4	63	675	1,590	2,337	78	293	1,020	1,780	2,447
Composition of gas: <i>a</i>	14.7	1.9	1.4	1.8	81.5	62.8	30.9	21.5	17.3
CO ₂	10.1	4.5	3.9	3.3	3.8	4.0	2.9	2.7
Illuminants.....	9.3	3.9	5.4	4.9	15.6	21.7	21.4	23.3	21.0
CO.....	63.1	61.4	40.5	35.6	2.4	11.7	27.4	19.6	19.3
CH ₄ , C ₂ H ₆ , etc.....	2.8	28.3	48.8	54.4	0	0	16.3	32.7	39.7
H.....	1.48	1.27	1.32	1.07	1.62	1.44	1.27	1.22	1.17
Value of n in C _n H _{2n+2}

a Computed to nitrogen and oxygen free basis.

TABLE 12.—*Early volatile products in second series of tests.*

[10 grams of air-dried coal heated to definite temperatures, 200° below that of furnace.]

	Coal No. 1.			Coal No. 3.			Coal No. 16.		
Temperature of furnace. ° C..	600.	750.	900.	600.	750.	900.	600.	750.	900.
Time heated.....minutes..	8.5	6.3	4.8	7.7	7.5	6.3	8.2	7.3	5.8
Tar.....per cent.		6.9	7.1		9.3	12.0		3.6	6.9
Water.....do.....		14.1	15.2		4.7	4.7		2.3	2.7
Gas at 25° C., cubic centi- meters.....	150	664	1,568	89	817	1,775	65	653	1,640
Composition of gas: ^a									
CO ₂	28.2	9.5	6.6	15.8	3.5	2.6	13.7	2.5	1.8
Illuminants.....	7.1	4.1	3.7	9.2	6.9	7.0	8.6	4.9	4.5
CO.....	16.5	15.4	15.9	7.1	5.5	7.4	6.2	3.7	4.6
CH ₄ , C ₂ H ₆ , etc.....	45.7	48.4	32.3	60.8	61.4	43.5	63.8	61.5	44.0
H.....	2.5	22.6	41.5	7.1	22.7	39.5	7.7	27.4	45.1
Value of n in C _n H _{2n+2}	1.38	1.21	1.19	1.53	1.27	1.18	1.60	1.24	1.15

	Coal No. 11.			Coal No. 18.			Coal No. 10.		
Temperature of furnace. ° C..	600.	750.	900.	600.	750.	900.	600.	750.	900.
Time heated.....minutes..	10.1	6.5	3.7	6.8	5.9	5.0	6.6	6.7	6.0
Tar.....per cent.		3.8	3.3		11.6	10.8		11.6	12.1
Water.....do.....		21.2	22.6		11.2	11.9		4.9	4.9
Gas at 25° C., cubic centi- meters.....	407	1,056	2,015	217	934	1,925	136	985	1,983
Composition of gas: ^a									
CO ₂	59.8	30.5	18.9	28.9	10.9	8.2	12.7	4.1	2.7
Illuminants.....	3.7	3.1	2.5	9.3	8.3	8.6	9.7	8.0	8.2
CO.....	20.3	20.7	23.6	17.5	17.3	18.2	6.2	5.8	7.6
CH ₄ , C ₂ H ₆ , etc.....	14.7	24.4	17.6	40.0	44.9	32.1	61.6	57.0	40.5
H.....	1.5	21.3	37.4	4.3	18.6	32.9	9.8	25.1	41.0
Value of n in C _n H _{2n+2}	1.52	1.25	1.29	1.34	1.29	1.26	1.66	1.26	1.19

^a Computed to oxygen and nitrogen free basis.

TABLE 13.—*Volumes of various gases produced in second series of tests.*

TEMPERATURE OF FURNACE, 600°; OF COAL, 400°.

No. of coal.....	16.	3.	10.	1.	18.	11.
Time heated.....minutes..	8.2	7.7	6.6	8.5	6.8	10.1
CO ₂	9	14	17	42	63	243
CO.....	4	6	8	25	38	83
Illuminants.....	6	8	13	11	20	15
CH ₄ , C ₂ H ₆ , etc.....	41	54	84	68	87	60
H.....	5	7	14	4	9	6
Value of n in C _n H _{2n+2}	1.60	1.53	1.66	1.38	1.34	1.52

TEMPERATURE OF FURNACE, 750°; OF COAL, 550°.

Time heated.....minutes..	7.3	7.5	6.7	6.3	5.9	6.5
CO ₂	16	29	40	63	102	321
CO.....	24	45	57	102	161	219
Illuminants.....	32	56	79	27	78	33
CH ₄ , C ₂ H ₆ , etc.....	402	502	562	322	419	258
H.....	179	185	247	150	174	225
Value of n in C _n H _{2n+2}	1.24	1.27	1.26	1.21	1.29	1.25

TEMPERATURE OF FURNACE, 900°; OF COAL, 700°.

Time heated.....minutes..	5.8	6.3	6.0	4.8	5.0	3.7
CO ₂	29	46	54	103	158	381
CO.....	75	131	150	249	350	476
Illuminants.....	74	125	163	59	166	50
CH ₄ , C ₂ H ₆ , etc.....	722	772	803	506	618	355
H.....	740	701	813	651	633	763
Value of n in C _n H _{2n+2}	1.15	1.18	1.19	1.19	1.26	1.29

CONCLUSIONS FROM RESULTS ON EARLY VOLATILE MATTER.

The tabulated and platted data given above lead to several general conclusions.

The early volatile products from the Illinois and Wyoming coals contain large proportions of inert constituents and of carbon monoxide. At the lower temperatures also they contain more combustible gases than those from the eastern coals. Smoky constituents (shown in figs. 4 and 8) are greatest from the Connellsville coal and the West Virginia and Wyoming gas coals. Higher hydrocarbons, such as ethane, are produced in greatest abundance from the eastern coals; the quantity produced rises to a maximum at about 800°, then rapidly falls on account of decomposition by heat. At furnace temperatures of 500° and 600° these higher hydrocarbons constitute about 50 per cent of the total methane hydrocarbons.

On the other hand, when the heating is continued only to a certain temperature in the coal, as in the second series of tests above (Tables 12 and 13), the quantities of higher hydrocarbons increase continuously as a higher furnace temperature is used, for the time of heating grows less.

Coals of the low-volatile bituminous type, represented by Pocahontas coal, produce hydrogen abundantly on heating and also large amounts of methane hydrocarbons.

It is indicated that smokeless combustion is more difficult with coals of the Connellsville and the West Virginia "gas" types than with the southern Illinois and the Wyoming subbituminous types. On the other hand, certain western coals like that of Diamondville, Wyo., produce a rich smoky volatile matter at moderate temperatures in larger quantities than the eastern smoky coals. Coals of this Diamondville type, of which there are representatives in several different localities in the West, show every indication of being valuable for the manufacture of illuminating gas and by-products.

It is evident that the geologically older Appalachian coals, as compared to the younger western coals, contain a larger amount of bitumen or substances which readily liberate methane and ethane hydrocarbons and hydrogen. The western coals, on the other hand, in inverse ratio to their geologic age, produce larger amounts of CO₂, CO, and water. The readiness with which CO₂ is liberated in large amounts even at the lower temperatures (300° to 500°) indicates the presence of compounds having the direct carbon-oxygen linking, such as the complex alcohols, aldehydes, or acids.

VOLATILE MATTER AT ORDINARY TEMPERATURES AND AT 105° C.

In connection with experiments on losses during storage of coal, the writers have noted the accumulation, in sealed bottles containing coal, of considerable amounts of methane and, in some cases, also,

of small amounts of CO_2 . Parr and Wheeler^a have previously noted this accumulation of combustible gas from Illinois coals in sealed bottles, but did not collect or analyze the gas. The present writers hope to publish in another bulletin the results of a series of experiments on the storage of coal, in which will be embodied a large amount of data on the accumulation of gas.

These experiments have shown also a remarkably rapid and long-continued absorption of oxygen by coal in storage, with some variation among coals in respect to the amount and rapidity of the absorption. R. T. Chamberlin in his "Notes on explosive mine gases and dusts,"^b previously cited, demonstrates the continuous formation and accumulation of methane from coal in mines, and the rapid absorption by coal dust of oxygen from the air without forming CO_2 .

A series of experiments on the direct weighing of the products driven off in drying powdered coal for two hours at 105°C . showed slight losses of CO_2 (0.1 to 0.4 per cent) with coals from southern Illinois and the Sheridan field, Wyoming, but only traces of hydrocarbons.

TEMPERATURE IN THE "OFFICIAL" VOLATILE-MATTER DETERMINATION.

One gram of powdered coal was heated for seven minutes in the usual manner prescribed for the "official" volatile-matter determination, except that a hole was made in the crucible cover and a thermocouple inserted just under the surface of the coal. With coal No. 1 (Illinois) the maximum temperature (830°C .) was reached in three minutes; with coal No. 3 (Connellsville) the maximum (838°C .) was reached in three minutes and a half.

CALCULATION OF THE HEAT VALUE OF COAL FROM ITS ULTIMATE ANALYSIS.

The experimental results given in the preceding pages show conclusively that in the process of breaking down under the influence of heat the coal substance gives up its oxygen partly in the form of carbon-oxygen compounds and partly as the hydrogen-oxygen compound water. Some recent work by Vignon in Europe supports this conclusion.^c The figures demonstrating this point are given again below in more compact form.

^a Bull. 17, Univ. Illinois Eng. Exper. Sta., 1907, p. 33.

^b Bull. U. S. Geol. Survey No. 383, 1909.

^c Vignon, L., Bull. Soc. chim., 4th ser., vol. 3, p. 109.

TABLE 14.—*Oxygen relations in volatile matter.*

[Values are percentages of air-dried coal.]

Coal.	Per cent of oxygen compounds in volatile matter.			Oxygen in CO and CO ₂ .	Oxygen in water.	Total oxygen in dry coal.
	CO ₂ . ^a	CO.	Water of constitution.			
No. 16 (Pocahontas):						
400-gram tests.....	0.44	1.21	0.1	1.01	0.09	3.18
10-gram tests.....	.90	1.74	1.5	1.65	1.33	3.18
No. 3 (Connellsville):						
400-gram tests.....	.72	3.7	3.29	5.23
10-gram tests.....	1.04	2.33	3.5	2.08	3.10	5.23
No. 1 (Zeigler, Ill.):						
10-gram tests.....	1.66	4.90	6.7	4.01	5.95	9.12
No. 11 (Sheridan, Wyo.; air dried):						
400-gram tests.....	8.60	6.90	7.5	10.19	6.67	16.63
10 gram tests.....	8.80	8.10	11.03	16.63

^a There is a possibility of the formation of CO₂ in slight amount from the oxygen of air in contact with the coal at the beginning of a test. On the assumption that 500 cubic centimeters of air is in contact with the coal, there could be formed, if all its oxygen entered into CO₂, only 0.28 gram of CO₂, or 0.07 per cent, on 400 grams of coal.

Dulong's calculation of heat value from the ultimate analysis assumes that all of the oxygen of the coal combines with hydrogen of the coal during combustion, thereby neutralizing, so to speak, the calorific value of an amount of hydrogen equal to $O \div 8$. Dulong's calculation, as is well known, gives for many coals less calories than are shown by experimental determination. The coals exhibiting these discrepancies are usually medium and low grade coals, high in oxygen, which, as has been shown above, give up their oxygen in large part combined with carbon instead of with hydrogen.

By combining with carbon instead of with hydrogen in the coal the oxygen exercises less anticalorific influence on the efficiency of the coal, as 1 gram of oxygen in combining with carbon to CO₂ neutralizes three-eighths of a gram of carbon, or 3,030 calories; in combining with carbon to CO it partly neutralizes three-fourths of a gram of carbon, thus neutralizing $\frac{3}{4} \times 2,417 = 1,813$ calories; whereas 1 gram of oxygen in combining with hydrogen to H₂O neutralizes one-eighth gram of hydrogen, or $\frac{1}{8} \times 34,460 = 4,308$ calories. The anticalorific influence of a unit of oxygen in forming CO₂ or CO is therefore approximately 70 per cent or 42 per cent, respectively, of its influence when forming water.

Before the Geological Society of Washington^a David White called attention to the uniform anticalorific influence which oxygen has in coal and based partly on this factor a scheme for the classification of coals. In a later publication^b he concludes from a study of analytical data (on air-dried coal) that oxygen and ash appear to have nearly the same anticalorific value in coal. If this conclusion is correct, and

^a Science, vol. 27, 1908, p. 537.
^b White, David, The effect of oxygen in coal: Bull. U. S. Geol. Survey No. 383, pp. 8-21 and 36-37.

oxygen, like ash, has merely a diluting effect, its possible neutralizing effect in reducing the availability of hydrogen and carbon is not to be considered. A conclusion, however, that is probably nearer the truth is that oxygen has in some degree a neutralizing effect on hydrogen and carbon, since it is undoubtedly in chemical union with these elements in the coal and appears in combination with them in the volatile products. This conclusion is supported by analytical data on moisture-free coal. Oxygen has not, on the other hand, as great a neutralizing effect as is assigned to it by Dulong's formula, since, as demonstrated in the present paper, a portion of the oxygen neutralizes carbon rather than hydrogen.

If the heat values of an Illinois coal (No. 19) and of a Wyoming coal (No. 11) are calculated by Dulong's formula and by formulas based on the distribution of oxygen between H₂O, CO, and CO₂ according to the experimental results herein set forth, the following values are found:

Composition and heat value of Illinois and Wyoming coals.

	Illinois (No. 19). ^a	Wyoming (No. 11). ^b
Composition (water free):		
Ash.....	6.16	5.56
Carbon.....	76.96	68.90
Hydrogen.....	4.49	4.56
Nitrogen.....	1.52	1.51
Sulphur.....	.52	.51
Oxygen.....	10.35	18.96
Calories:		
Dulong's calculation.....	7,322	6,333
Modified calculation.....	7,453	6,524
Determined.....	7,536	6,582

^a From Zeigler, Franklin County, Ill.
^b From Dietz, near Sheridan, Wyo. (subbituminous).

The formulas used for the modified calculation are the following:
Illinois type:
Calorific value = 8,080(C - 0.120 × O) + 34,460(H - 0.063 × O) + 2,250S.
Wyoming type:
Calorific value = 8,080(C - 0.182 × O) + 34,460(H - 0.050 × O) + 2,250S.

DETAILED DATA OF INDIVIDUAL TESTS.

Full details of the results on which the conclusions presented in this bulletin are based are given in the subjoined tables:

TABLE 15.—Results of by-product tests of 400 grams of coal.

Coal No.	Test No.	Coke (per cent).	Tar (per cent).	Water (per cent).	Ammonia (pounds of sulphate per ton).	CO ₂ (per cent).	H ₂ S (per cent).	Gas at 0° C. and 30 inches of mercury (cubic feet per ton).
16	33	79.1	7.2	1.0	13.2	0.44	0.08	10,180
16	34	79.1	7.2	1.5	12.5	.43	.06	9,210
3	39	73.5	-----	-----	25.0	.71	.28	8,650
3	41	70.8	13.7	2.4	22.8	.72	.21	8,670
3	42	70.3	-----	-----	22.0	-----	-----	8,080
3	43	70.8	11.3	5.1	22.8	-----	-----	7,840
3	47	72.2	10.5	5.6	25.5	-----	-----	8,000
3	50	70.5	9.8	6.4	24.4	-----	-----	7,800
^a 3	48	67.1	8.5	14.1	24.1	-----	-----	6,960
^a 3	49	66.0	9.8	12.5	24.5	-----	-----	6,325
23	31	63.1	12.3	11.0	26.4	1.20	.47	8,400
23	32	63.1	11.5	10.3	24.1	1.19	.44	8,400
11	22	44.8	6.9	-----	28.4	8.10	.08	7,850
11	24	44.4	8.2	26.5	25.5	8.22	.07	7,890
11	25	44.9	6.5	27.0	25.9	-----	-----	-----
11	40	45.0	6.8	29.0	29.1	8.03	.10	7,760
^b 11	36	52.9	5.3	19.0	28.2	8.62	.12	8,540
^b 11	37	53.1	5.6	19.0	25.1	8.20	.10	7,790
25	51	58.4	12.1	11.5	25.8	3.07	.25	7,640
25	53	58.7	12.4	12.0	26.7	3.20	.22	7,600
46	54	63.3	9.9	10.8	25.5	1.86	.30	7,950
46	57	64.4	10.6	9.2	27.1	1.73	-----	7,930

^a Coal moistened to 9.6 per cent of moisture.
^b Air-dried coal, 11.5 per cent of moisture.

TABLE 16.—*Analyses of samples of gas obtained successively during by-product tests.*

[The analyses under each test are stated in order in which they were made. Unless otherwise specified CO₂ was removed from gas during test.]

Coal and test Nos.	Composition of gas.							Value of $\frac{n}{n+1} \ln$ $C_n H_{2n+2}$.
	CO ₂ .	Illumi- nants.	O.	CO.	CH ₄ , C ₂ H ₆ , etc.	H.	N.	
Coal 16:								
Test 33.....	0	3.5	0.5	2.8	38.2	42.7	12.3	(a)
	0	1.6	.4	4.0	31.0	62.5	.5	(a)
	0	.5	.0	.8	5.8	87.9	5.0	(a)
	0	0	.2	.8	3.1	88.3	7.6	(a)
Test 34.....	.2	3.4	.4	0	59.6	31.7	.7	(a)
	0	2.0	.2	4.4	33.0	57.5	2.9	(a)
	0	0	.2	1.0	5.9	87.7	5.2	(a)
	0	0	.3	.9	3.7	89.1	6.0	(a)
Coal 3:								
Test 39.....	0	5.1	.5	6.1	43.5	37.6	7.2	1.25
	0	2.4	.3	6.3	19.3	66.7	5.0	1.18
Test 41.....	0	5.7	5.4	4.1
	0	4.7	.5	5.8	43.4	42.3	2.3	1.19
	0	0	0	3.4	6.8	84.5	5.3
	.4	0	.2	3.2	4.7	85.4	6.1
Test 42.....	^b 3.4	6.2	1.6	5.2	49.5	22.0	12.1	1.34
	2.1	3.8	.5	6.4	39.0	45.4	2.8	1.18
	.6	.2	.4	3.6	8.3	83.3	3.6
	0	.4	0	2.4	8.5	84.3	4.4
Test 43.....	4.2	5.5	0	5.3	51.1	25.8	8.1	1.31
	2.1	4.2	0	6.3	36.3	47.5	3.6	1.22
	.4	.2	0	5.8	12.0	79.3	2.3
Test 47.....	^b 3.3	5.0	.3	5.3	55.4	27.4	3.4	1.26
Test 48.....	3.7	4.6	.8	5.4	51.6	29.9	4.0	1.28
	2.4	3.0	.1	5.4	35.7	51.7	1.7	1.14
	.5	.5	0	2.8	9.5	83.5	3.2
Test 49.....	^b 4.2	5.4	.7	5.1
	2.9	3.5	.4	6.5	46.4	38.4	1.9	1.21
	1.4	.7	0	4.6	17.0	73.7	2.6
Coal 23:								
Test 31.....	0	5.1	.8	7.1	34.5	35.5	17.0	(a)
	0	4.5	0	9.4	32.4	50.9	2.8	(a)
	0	0	.1	5.7	7.3	80.4	6.5	(a)
	0	0	0	3.2	3.0	81.9	11.9	(a)
Test 32.....	0	4.4	.5	6.8	57.7	27.1	3.5	(a)
	0	4.2	.6	9.2	(a)
	0	.1	0	7.3	13.8	76.4	2.4	(a)
	0	0	0	4.3	6.2	80.7	9.0	(a)
Coal 11:								
Test 22.....	.9	3.5	.2	12.3	20.4	50.0	12.9	(a)
	5.8	1.6	.3	24.2	9.3	49.5	9.3	(a)
	2.6	0	.4	22.9	6.5	57.4	10.2	(a)
Test 24.....	4.0	3.4	.2	12.1	22.1	51.7	6.5	(a)
	5.4	1.8	.2	21.9	18.4	49.9	2.4	(a)
	.3	.1	.2	27.5	7.1	55.6	9.2	(a)
Test 25.....	7.4	2.6	.3	10.3	20.2	52.5	6.7	(a)
	10.0	2.2	.4	17.9	19.0	47.3	3.2	(a)
	5.6	.2	.2	27.6	5.9	50.9	9.6	(a)
Test 40.....	1.4	4.8	2.2	19.2	29.8
	5.2	1.6	.3	22.4	12.4	50.3	7.8
Coal 11 (air dried):								
Test 36.....	11.7	3.5	.5	17.7	37.2	23.4	6.0	(a)
	12.2	2.6	0	19.5	22.4	40.8	2.5	(a)
	2.4	1.0	.4	18.4	14.2	57.1	6.5	(a)
	.1	0	.3	10.2	9.5	68.0	11.9	(a)
Test 37.....	14.0	3.7	.2	16.2	33.5	25.7	6.7	(a)
	11.4	2.9	.3	19.9	23.9	38.3	3.3	(a)
	0	0	0	22.2	12.3	58.0	7.8	(a)
Coal 25:								
Test 51.....	.4	7.8	0	12.6	52.0	21.3	5.9	1.33
	.8	9.2	0	14.8	35.2	36.6	3.4	1.33
	.5	.9	0	13.9	9.2	68.8	6.7	1.34
	.5	.6	.3	7.5	5.7	76.4	9.0	1.71
Coal 46:								
Test 54.....	0	9.1	0	13.4	41.9	30.3	5.3	1.40
	1.5	9.5	.2	13.6	25.7	46.3	3.2	1.33
	0	.4	.2	10.0	5.3	77.8	6.3	1.68
Test 57.....	1.3	7.2	0	13.3	45.2	32.2	.8	1.31
	0	6.3	.4	12.9	26.1	51.4	2.9	1.25
	.2	.5	.2	8.2	6.9	78.2	5.8	1.48

^a Not determined, as H was not separately determined.

^b CO₂ not removed during test.

TABLE 17.—Analyses of total gas from by-product tests.

Coal No.	Test No.	Composition of gas. ^a					Value of n in C _n H _{2n+2} .
		Illuminants.	CO.	CH ₄ , C ₂ H ₆ , etc.	H.	N.	
16	33	1.8	3.1	26.0	69.0	.1	(b)
16	34	1.0	3.3	26.8	66.5	2.4	(b)
3	39	3.5	5.2	26.4	60.4	4.5	1.23
3	41	3.9	5.0	21.4	66.5	3.3	1.46
3	42	3.3	5.2	29.3	59.9	2.3	1.19
3	43	3.3	4.9	30.1	58.8	2.9	1.18
3	47	2.7	5.2	30.3	58.1	3.7	1.26
3	50	2.7	5.2	29.3	61.0	1.8	1.29
3	48	2.9	5.0	33.3	58.3	.5	1.12
3	49	2.7	5.4	34.7	53.2	4.0	1.22
23	31	3.0	7.3	29.7	56.3	3.7	(b)
23	32	2.9	7.5	22.8	57.3	9.5	(b)
11	22	2.0	19.9	19.0	53.9	5.2	(b)
11	24	1.9	20.0	18.9	53.7	5.5	(b)
11	40	2.6	17.8	18.1	54.0	7.5	1.18
c11	36	2.5	21.2	21.4	51.6	3.3	(b)
c11	37	2.6	21.6	23.7	47.0	5.1	(b)
25	51	5.8	14.0	27.4	47.7	5.1	1.38
25	53	5.6	15.9	27.0	47.6	3.9	1.25
46	54	6.3	12.8	24.7	51.6	4.6	1.32
46	57	4.6	11.9	25.8	53.9	3.8	1.25

^a Reduced by calculation to CO₂ and air-free basis.
^b Not determined, as H was not separately determined.
^c Air-dried coal.

TABLE 18.—Total gas obtained from 10 grams of air-dried coal.

COAL NO. 1 (ZEIGLER, ILL.).

Temperature of furnace.....°C..	500.		600.		700.	
Test No.....	60	226	71	78	68	81
Highest temperature in coal.....°C..	390	490	470	580	575
Time to reach highest temperature, minutes.....	20	17	20	16	18
Gas at 25° C.....cubic centimeters..	130	264	570	500	965	990
Composition of gas: As collected—						
CO ₂	7.5	10.7	4.8	5.1	4.2	5.0
Illuminants.....	2.0	3.1	3.0	3.4	2.5	3.4
O.....	1.8	.5	.5	.3	.7	.4
CO.....	4.8	8.3	10.7	10.0	17.7	13.0
CH ₄ , C ₂ H ₆ , etc.....	11.3	32.2	37.3	33.2	33.9	26.7
H.....	.0	4.4	8.9	12.0	17.8	21.1
N.....	72.6	40.8	34.8	36.0	23.2	30.4
Computed to N and O free basis—						
CO ₂	29.3	18.2	7.4	8.0	5.5	7.2
Illuminants.....	7.8	5.2	4.6	5.3	3.3	4.9
CO.....	18.8	14.2	16.5	15.7	23.3	18.8
CH ₄ , C ₂ H ₆ , etc.....	44.1	54.9	57.7	52.2	44.5	38.6
H.....	.0	7.5	13.8	18.8	23.4	30.5
Value of n in C _n H _{2n+2}	1.48	1.36	1.21	1.36	1.18	1.23

TABLE 18.—Total gas obtained from 10 grams of air-dried coal—Continued.

COAL NO. 1 (ZEIGLER, ILL.)—Continued.

Temperature of furnace.....°C..	800.		900.		1,000.	1,100.
Test No.....	85	93	88	97	90	99
Highest temperature in coal.....°C..	679	691	797	^a 832	920	1,026
Time to reach highest temperature, minutes.....	12	12	10	8	7	6
Gas at 25° C.....cubic centimeters..	1,500	1,600	2,290	2,380	2,700	3,120
Composition of gas:						
As collected—						
CO ₂	3.0	3.4	2.0	2.4	2.2	1.6
Illuminants.....	3.0	2.4	3.2	2.4	3.1	3.5
O.....	.4	.2	.3	1.0	1.5	.3
CO.....	14.0	13.9	13.6	13.2	12.5	14.0
CH ₄ , C ₂ H ₆ , etc.....	25.0	32.1	24.0	25.1	19.2	16.9
H.....	35.4	33.3	45.0	45.4	46.0	51.2
N.....	19.2	14.7	11.9	10.5	15.5	12.5
Computed to N and O free basis—						
CO ₂	3.7	4.0	2.3	2.7	2.7	1.8
Illuminants.....	3.7	2.8	3.7	2.7	3.7	4.0
CO.....	17.5	16.3	15.5	14.9	15.1	16.1
CH ₄ , C ₂ H ₆ , etc.....	31.1	37.8	27.3	28.4	23.1	19.4
H.....	44.0	39.1	51.2	51.3	55.4	58.7
Value of n in C _n H _{2n+2}	1.17	1.15	1.26	1.18	1.18	1.23

^a Test run in air instead of in nitrogen.

COAL NO. 3 (CONNELLSVILLE, PA.).

Temperature of furnace.....°C..	500.		600.		700.	
Test No.....	61	227	79	84	77	82
Highest temperature in coal.....°C..	390	-----	487	478	577	577
Time to reach highest temperature.....minutes..	24	-----	14	15	13	17
Gas at 25° C.....cubic centimeters..	150	172	730	705	1,280	1,160
Composition of gas:						
As collected—						
CO ₂	3.8	4.8	2.8	2.6	2.6	1.8
Illuminants.....	1.8	3.7	4.4	4.6	3.5	3.0
O.....	3.1	.8	.8	.5	.1	.8
CO.....	1.8	2.4	4.6	3.1	4.2	4.8
CH ₄ , C ₂ H ₆ , etc.....	9.5	34.0	43.9	38.8	41.4	42.4
H.....	.0	3.9	13.2	10.6	23.5	22.5
N.....	80.0	50.4	30.3	39.8	24.7	24.7
Computed to N and O free basis—						
CO ₂	22.0	9.9	4.0	4.4	3.8	2.5
Illuminants.....	10.6	7.6	6.3	7.8	4.5	4.1
CO.....	10.6	5.0	6.6	5.3	5.6	6.9
CH ₄ , C ₂ H ₆ , etc.....	56.8	69.7	64.0	64.9	55.1	56.6
H.....	0	7.8	19.1	17.6	31.0	29.9
Value of n in C _n H _{2n+2}	1.87	1.50	1.39	1.35	1.31	1.23

Temperature of furnace.....°C..	800.		900.	1,000.	1,100.
Test No.....	87	94	89	92	106
Highest temperature in coal.....°C..	689	-----	810	922	1,008
Time to reach highest temperature.....minutes..	11	-----	9	7	5
Gas at 25° C.....cubic centimeters..	1,685	1,760	2,080	2,900	3,530
Composition of gas:					
As collected—					
CO ₂	1.6	2.0	.8	1.0	1.0
Illuminants.....	3.8	3.6	3.5	4.0	4.6
O.....	.5	.2	3.7	.2	.3
CO.....	6.2	6.4	5.4	5.6	6.6
CH ₄ , C ₂ H ₆ , etc.....	40.9	40.5	24.2	25.9	23.9
H.....	34.2	33.9	39.0	52.9	54.8
N.....	12.8	13.4	23.4	10.4	8.8
Computed to N and O free basis—					
CO ₂	1.7	2.3	1.1	1.2	1.0
Illuminants.....	4.7	4.2	4.8	4.6	5.2
CO.....	7.1	7.4	7.4	6.4	7.3
CH ₄ , C ₂ H ₆ , etc.....	47.1	46.9	33.2	29.0	26.3
H.....	39.4	39.2	53.5	58.8	60.2
Value of in C _n H _{2n+2}	1.24	1.18	1.22	1.11	1.15

TABLE 18.—*Total gas obtained from 10 grams of air-dried coal—Continued.*
COALS NO. 16 (POCAHONTAS, VA.) AND NO. 11 (DIETZ, WYO.).

	Coal No. 16.					Coal No. 11.		
Temperature of furnace.....°C..	500.		700.		1,000.	500.	700.	1,000.
Test No.....	229	230	96	100	107	228	101	104
Highest temperature in coal.....°C..			612	617	920		600	920
Time to reach highest temperature, minutes.....			13	14	8		10	6
Gas at 25° C.....cubic centimeters..	240	236	1,190	1,175	3,230	517	1,300	3,650
Composition of gas:								
As collected—								
CO ₂	2.8	3.0	1.0	1.2	.4	39.8	17.9	9.4
Illuminants.....	2.8	2.8	2.8	2.8	3.4	2.7	2.9	4.1
O.....	.8	.7	.4	.4	.4	.2	.3	.5
CO.....	2.3	1.9	4.2	4.0	4.2	14.4	17.7	20.2
CH ₄ , C ₂ H ₆ , etc.....		38.4	45.0	44.2	24.5	13.9	24.2	14.7
H.....		8.3	27.5	28.8	59.0	2.5	19.6	42.1
N.....		44.9	19.1	18.6	8.1	26.5	17.4	9.0
Computed to N and O free basis—								
CO ₂		5.5	1.3	1.5	.4	54.3	21.7	10.4
Illuminants.....		5.2	3.5	3.5	3.7	3.7	3.5	4.5
CO.....		3.5	5.2	4.9	4.6	19.6	21.5	22.3
CH ₄ , C ₂ H ₆ , etc.....		70.6	55.9	54.6	26.8	18.9	29.4	16.3
H.....		15.2	34.1	35.5	64.5	3.5	23.9	46.5
Value of n in C _n H _{2n+2}		1.46	1.17	1.21	1.13	1.55	1.19	1.25

TABLE 19.—*Early volatile products from ten minutes' heating of 10 grams of air-dried coal.*

COAL NO. 1 (ZEIGLER, ILL.).

Temperature of furnace.....°C..	500.	600.		700.		800.		900.
Test No. <i>a</i>	59	69	73	62	231	76	83	132
Highest temperature in coal.....°C..	345	445	435	550	540	670	689	
Tar.....per cent.....		6.3	7.1	7.9	8.5	9.7		9.1
Water.....do.....		11.8	12.7	13.9	13.3	13.5		14.4
Gas at 25° C.....cubic centimeters..	90	175	171	485	800	1,224	1,280	2,240
Composition of gas:								
As collected—								
CO ₂	5.0	7.8	7.7	6.4	7.5	3.2	3.4	3.3
Illuminants.....	0	3.4	3.5	3.9	2.8	3.2	3.2	2.9
O.....	2.6	.9	.3	.9	.3	.2	.3	.6
CO.....	1.8	6.3	8.0	10.4	13.1	14.6	13.3	13.0
CH ₄ , C ₂ H ₆ , etc.....	2.7	22.6	18.3		36.9		29.5	26.7
H.....	0	2.3	.4		19.6		29.5	42.9
N.....	87.9	56.7	61.8		19.8		20.8	10.6
Computed to O and N free basis—								
CO ₂	52.7	18.5	20.3		9.4		4.3	3.7
Illuminants.....	0	8.0	9.2		3.5		4.1	3.3
CO.....	18.9	14.9	21.1		16.4		17.0	14.6
CH ₄ , C ₂ H ₆ , etc.....	28.4	53.3	48.3		46.2		37.3	30.1
H.....	0	5.3	1.1		24.5		37.3	48.3
Value of n in C _n H _{2n+2}		1.48	1.62		1.23		1.18	1.09

a Number of test applies to test for gas only.

TABLE 19.—Early volatile products from ten minutes' heating of 10 grams of air-dried coal—Continued.

COAL NO. 3 (CONNELLSVILLE, PA.).

Temperature of furnace.....°C..	500.	600.			700.
Test No.....	66	70	72	75	64
Highest temperature in coal.....°C..	335	455	452	415	565
Tar.....per cent.....		5.1	5.3		12.6
Water.....do.....		3.1	2.7		3.2
Gas at 25° C.....cubic centimeters..	8	162	233	176	668
Composition of gas:					
As collected—					
CO ₂		3.2	3.0	3.2	2.6
Illuminants.....		4.2	4.0	4.3	5.8
O.....		.5	.9	.6	.3
CO.....		2.9	2.9	3.2	3.7
CH ₄ , C ₂ H ₆ , etc.....		23.6	39.1	30.8	
H.....		2.6	.3	.0	
N.....		63.0	49.8	57.9	
Computed to O and N free basis—					
CO ₂		8.8	6.1	7.7	
Illuminants.....		11.5	8.1	10.4	
CO.....		8.0	5.9	7.7	
CH ₄ , C ₂ H ₆ , etc.....		64.6	79.3	74.2	
H.....		7.1	.6	0.0	
Value of n in C _n H _{2n+2}		1.65	1.20	1.40	

Temperature of furnace.....°C..	700.		800.		900.
Test No.....	65	232	80	86	133
Highest temperature in coal.....°C..	555	565	695	679	
Tar.....per cent.....	10.6		12.9	13.5	12.5
Water.....do.....	2.7		4.2	3.8	4.7
Gas at 25° C.....cubic centimeters..		990	1,400	1,350	2,180
Composition of gas:					
As collected—					
CO ₂	1.7	2.3	1.6	1.0	2.2
Illuminants.....	4.7	5.0	5.3	4.5	4.8
O.....	3.0	.3	.7	.3	.4
CO.....	4.4	4.7	6.4	5.9	6.4
CH ₄ , C ₂ H ₆ , etc.....	35.4	47.3	36.0	30.1	31.9
H.....	13.5	22.8	27.6	31.7	45.0
N.....	37.3	17.6	22.4	26.5	9.3
Computed to O and N free basis—					
CO ₂	2.8	2.8	2.1	1.4	2.4
Illuminants.....	7.8	6.1	6.9	6.1	5.3
CO.....	7.4	5.7	8.3	8.1	7.1
CH ₄ , C ₂ H ₆ , etc.....	59.2	57.6	46.8	41.2	35.3
H.....	22.8	27.8	35.9	43.2	49.9
Value of n in C _n H _{2n+2}	1.50	1.31	1.25	1.41	1.19

COAL NO. 16 (POCAHONTAS, VA.).

Temperature of furnace.....°C..	500.	600.			700.	800.	900.	
Test No.....	124	119	120	122	103	115	127	131
Highest temperature in coal.....°C..					599			
Tar.....per cent.....	0.3	0.9	1.0		4.4	6.7	6.7	6.7
Water.....do.....	.8	1.2	1.3		1.7	2.1	2.8	2.7
Gas at 25° C.....cubic centimeters..	4	96	40	62	675	1,590	2,325	2,350
Composition of gas:								
As collected—								
CO ₂		3.6	2.8	3.0	1.4	1.1	1.2	1.6
Illuminants.....		2.8	1.6	2.2	3.2	3.1	3.2	3.0
O.....		.3	1.6	.5	1.6	.3	.2	.2
CO.....		2.2	1.8	1.9	2.8	4.3	4.6	4.4
CH ₄ , C ₂ H ₆ , etc.....		14.7	11.1	14.6	44.1	32.6		32.3
H.....		2.2	0	0	20.3	39.2		49.4
N.....		74.2	81.1	77.8	26.6	19.4		9.1
Computed to O and N free basis—								
CO ₂		14.1	16.2	13.8	1.9	1.4		1.8
Illuminants.....		11.0	9.2	10.1	4.5	3.9		3.3
CO.....		8.6	10.4	8.8	3.9	5.4		4.9
CH ₄ , C ₂ H ₆ , etc.....		57.7	64.2	67.3	61.4	40.5		35.6
H.....		8.6	0.0	0.0	28.3	48.8		54.4
Value of n in C _n H _{2n+2}		1.63	1.48	1.32	1.27	1.32		1.07

TABLE 19.—*Early volatile products from ten minutes' heating of 10 grams of air-dried coal—Continued.*

COAL NO. 11 (DIETZ, WYO.).

Temperature of furnace.....°C.	500.		600.		
Test No.....	121	123	116	117	118
Highest temperature in coal.....°C.					
Tar.....per cent.		2.0	3.0	1.8	
Water.....do.		14.5	22.0	20.0	
Gas at 25°C.....cubic centimeters.	94	63	350	270	260
Composition of gas:					
As collected—					
CO ₂	29.4	23.9	34.0	36.2	36.5
Illuminants.....	.4	0	2.2	2.1	2.2
O.....	.8	.5	.4	.4	.7
CO.....	5.6	4.6	14.0	11.6	11.5
CH ₄ , C ₂ H ₆ , etc.....	.4	1.1	9.8	5.6	4.7
H.....	0	0	0	0	0
N.....	63.4	69.9	39.6	44.1	44.4
Computed to O and N free basis—					
CO ₂	82.2	80.7	56.7	65.2	66.5
Illuminants.....	1.1	0	3.7	3.8	4.0
CO.....	15.6	15.6	23.3	20.9	20.9
CH ₄ , C ₂ H ₆ , etc.....	1.1	3.7	16.3	10.1	8.6
H.....	0	0	0	0	0
Value of n in C _n H _{2n+2}	1.25	2.00	1.22	1.48	1.62

Temperature of furnace.....°C.	700.	800.	900.		
Test No.....	105	114	126	128	130
Highest temperature in coal.....°C.	580				
Tar.....per cent.	8.6	8.3	9.8	10.0	
Water.....do.	18.1	18.7	24.8	23.9	
Gas at 25°C.....cubic centimeters..	1,020	1,780	2,400	2,350	2,590
Composition of gas:					
As collected—					
CO ₂	24.8	18.0	14.4	15.7	15.4
Illuminants.....	3.2	2.4	2.4	1.2	2.4
O.....	.2	.2	.3	.5	.2
CO.....	17.2	19.5	20.7	21.8	18.7
CH ₄ , C ₂ H ₆ , etc.....	22.0	16.4			17.1
H.....	13.1	27.3			35.3
N.....	19.5	16.2			10.9
Computed to O and N free basis—					
CO ₂	30.9	21.5			17.3
Illuminants.....	4.0	2.9			2.7
CO.....	21.4	23.3			21.0
CH ₄ , C ₂ H ₆ , etc.....	27.4	19.6			19.3
H.....	16.3	32.7			39.7
Value of n in C _n H _{2n+2}	1.27	1.22			1.17

TABLE 20.—*Early volatile products in second series of tests (heating 10 grams of air-dried coal to definite temperatures).*

COAL NO. 1 (ZEIGLER, ILL.).

Temperature of furnace.....°C..	600.		750.			900.		
Test No.....	155	157	166	167	168	174	175	189
Highest temperature in coal.....°C..	400	400	550	550	550	700	700	700
Time to reach highest temperature.....minutes..	8.7	8.3	7.0	6.0	7.0	5.0	5.0	4.5
Tar.....per cent..	(a)	6.6	7.2	7.0	7.2
Water.....do....	(a)	14.3	13.9	15.7	14.6
Gas at 25° C.....cubic centimeters..	149	152	632	696	663	1,480	1,545	1,680
Composition of gas:								
As collected—								
CO ₂	12.9	12.8	6.8	7.3	8.4	6.0	6.2	5.5
Illuminants.....	3.1	3.4	3.0	3.3	3.3	2.9	3.3	3.7
O.....	.5	.4	.2	.4	0	.5	.2	0
CO.....	7.1	7.9	11.9	12.3	11.9	14.6	13.8	14.3
CH ₄ , C ₂ H ₆ , etc.....	20.8	20.9	38.3	37.4	38.0	30.0	29.2	27.8
H.....	.3	2.1	17.9	17.9	16.7	39.1	34.7	37.7
N.....	55.3	52.5	21.9	21.4	21.3	6.9	12.6	11.0
Computed to O and N free basis—								
CO ₂	29.0	27.3	8.7	9.3	10.6	6.5	7.1	6.2
Illuminants.....	7.0	7.2	3.8	4.2	4.2	3.1	3.8	4.2
CO.....	16.1	16.9	15.3	15.8	15.1	15.8	15.9	16.1
CH ₄ , C ₂ H ₆ , etc.....	47.3	44.1	49.1	47.9	48.3	32.4	33.4	31.2
H.....	.6	4.5	23.1	22.8	21.8	42.2	39.8	42.3
Value of n in C _n H _{2n+2}	1.33	1.43	1.21	1.20	1.22	1.19	1.19	1.18

a Tar and water determinations not made at 600° in this series.

COAL NO. 3 (CONNELLSVILLE, PA.).

Temperature of furnace.....°C..	600.			750.			900.	
Test No.....	150	151	152	163	164	165	172	173
Highest temperature in coal.....°C..	400	400	400	550	550	550	700	700
Time to reach highest temperature.....minutes..	7.0	8.7	7.5	8.0	7.0	7.5	6.3	6.3
Tar.....per cent..	9.0	9.9	9.0	12.0	12.0
Water.....do....	5.0	4.3	4.8	4.5	4.9
Gas at 25° C.....cubic centimeters..	88	79	99	775	847	830	1,740	1,810
Composition of gas:								
As collected—								
CO ₂	5.4	5.8	4.9	3.3	2.4	2.7	2.1	2.5
Illuminants.....	3.6	2.8	3.0	5.5	5.5	5.5	6.2	6.4
O.....	0	.3	.6	.5	.1	.4	0	0
CO.....	2.1	2.2	2.9	4.6	4.6	4.1	6.2	7.1
CH ₄ , C ₂ H ₆ , etc.....	21.3	20.4	20.3	47.7	50.4	49.8	40.6	38.5
H.....	4.4	1.4	1.7	17.1	18.8	18.6	35.6	36.2
N.....	63.2	67.1	66.6	21.3	18.2	18.9	9.3	9.3
Computed to O and N free basis—								
CO ₂	14.6	17.8	14.9	4.1	3.0	3.3	2.3	2.8
Illuminants.....	9.9	8.5	9.1	7.1	6.8	6.8	6.9	7.1
CO.....	5.8	6.7	8.8	5.9	5.4	5.1	6.9	7.8
CH ₄ , C ₂ H ₆ , etc.....	57.8	62.7	62.0	60.1	62.2	61.8	44.7	42.4
H.....	11.9	4.3	5.2	22.8	22.6	23.0	39.2	39.9
Value of n in C _n H _{2n+2}	1.63	1.42	1.54	1.27	1.26	1.29	1.18	1.19

TABLE 20.—*Early volatile products in second series of tests (heating 10 grams of air-dried coal to definite temperatures)*—Continued.

COAL NO. 16 (POCAHONTAS).

Temperature of furnace.....°C..	600.			750.		900.	
Test No.....	153	156	159	161	162	176	177
Highest temperature in coal.....°C..	400	400	400	550	550	700	700
Time to reach highest temperature..minutes..	8.0	8.0	8.5	7.3	7.3	5.8	5.8
Tar.....per cent..				3.7	3.5	6.6	7.1
Water.....do.				2.2	2.3	2.9	2.5
Gas at 25° C.....cubic centimeters..	67	62	77	647	659	1,650	1,630
Composition of gas:							
As collected—							
CO ₂	3.4	2.6	4.0	1.9	1.8	1.6	1.5
Illuminants.....	2.0	2.2	2.1	3.7	3.9	4.1	4.0
O.....	.3	.3	.8	.6	.4	.5	0
CO.....	1.8	1.1	1.6	3.0	2.7	3.7	4.5
CH ₄ , C ₂ H ₆ , etc.....	16.1	13.5	16.5	48.2	46.8	39.2	39.2
H.....	1.0	3.4	1.1	21.2	21.2	39.8	40.5
N.....	75.4	76.9	73.9	21.4	23.2	11.1	10.3
Computed to O and N free basis—							
CO ₂	13.8	11.4	15.8	2.5	2.4	1.8	1.7
Illuminants.....	8.1	9.5	8.2	4.8	5.1	4.6	4.4
CO.....	7.3	5.0	6.3	3.9	3.5	4.2	5.0
CH ₄ , C ₂ H ₆ , etc.....	66.7	59.2	65.4	61.8	61.2	44.3	43.7
H.....	4.1	14.9	4.3	27.0	27.8	45.1	45.2
Value of n in C _n H _{2n+2}	1.54	1.71	1.55	1.21	1.27	1.15	1.15

COAL NO. 11 (DIETZ, WYO.).

Temperature of furnace.....°C..	600.		750.			900. ^a		
Test No.....	158	160	169	170	171	178	179	182
Highest temperature in coal.....°C..	400	400	550	550	550	700	700	700
Time to reach highest temperature.....minutes..	10.2	10.0	7.0	6.0	6.5	3.7	3.7	3.7
Tar.....per cent..			3.8	3.8		2.9	3.7	
Water.....do.			21.0	21.3		23.1	22.1	
Gas at 25° C.....cubic centimeters..	408	406	1,048	1,018	1,100	1,990	2,050	2,000
Composition of gas:								
As collected—								
CO ₂	42.0	41.6	25.6	25.8	25.6	17.5	16.9	17.0
Illuminants.....	2.8	2.4	2.6	2.6	2.5	2.3	2.1	2.3
O.....	.1	.4	.4	.3	.2	.2	.4	.2
CO.....	14.5	14.0	17.3	17.7	17.3	21.5	21.4	21.2
CH ₄ , C ₂ H ₆ , etc.....	10.7	10.1	21.5	20.3	19.7	17.5	14.7	15.8
H.....	1.2	.9	17.4	18.0	18.2	33.7	34.5	33.4
N.....	28.7	30.6	15.2	15.3	16.5	7.3	10.0	10.1
Computed to O and N free basis—								
CO ₂	59.2	60.3	30.3	30.5	30.7	18.9	18.9	18.9
Illuminants.....	3.9	3.5	3.1	3.1	3.1	2.5	2.3	2.6
CO.....	20.4	20.3	20.5	20.9	20.8	23.2	23.9	23.6
CH ₄ , C ₂ H ₆ , etc.....	14.8	14.6	25.5	24.0	23.6	18.9	16.4	17.6
H.....	1.7	1.3	20.6	21.5	21.8	36.5	38.5	37.3
Value of n in C _n H _{2n+2}	1.48	1.56	1.22	1.25	1.29	1.21	1.39	1.28

^a Tests on coal No. 11 at 900° were run on coarsely-powdered material (between 10 and 20 mesh) in order to avoid mechanical loss.

TABLE 20.—*Early volatile products in second series of tests (heating 10 grams of air-dried coal to definite temperatures)*—Continued.

COAL NO. 18 (DIAMONDVILLE, WYO.)

Temperature of furnace.....°C..	600.		750.		900.	
Test No.....	225	225a	185	186	180	181
Highest temperature in coal.....°C..	400	400	550	550	700	700
Time to reach highest temperature .. minutes..	6.5	7.0	5.5	6.2	5.0	5.0
Tar.....per cent.....			11.6	11.6	11.2	10.4
Water.....do.....			11.3	11.0	11.6	12.2
Gas at 25°C.....cubic centimeters..	228	206	943	925	1,900	1,950
Composition of gas: As collected—						
CO ₂	14.7	15.7	9.5	8.7	7.5	7.2
Illuminants.....	5.1	4.7	7.2	6.5	7.7	8.0
O.....	.4	.8	.3	.6	.1	.1
CO.....	9.8	8.6	14.3	14.5	16.7	16.1
CH ₄ , C ₂ H ₆ , etc.....	22.9	19.3	37.9	36.6	29.2	28.5
H.....	2.0	2.6	14.9	16.0	28.9	30.5
N.....	45.1	48.3	15.9	17.1	9.9	9.6
Computed to O and N free basis—						
CO ₂	27.0	30.8	11.3	10.5	8.3	8.0
Illuminants.....	9.4	9.2	8.6	7.9	8.5	8.8
CO.....	18.0	16.9	17.1	17.6	18.6	17.8
CH ₄ , C ₂ H ₆ , etc.....	42.0	37.9	45.2	44.5	32.5	31.6
H.....	3.6	5.2	17.8	19.5	32.1	33.8
Value of n in C _n H _{2n+2}	1.55	1.23	1.26	1.31	1.23	1.28

COAL NO. 10 (PAGE, W. VA.)

Temperature of furnace.....°C..	600.		750.			900.	
Test No.....	224	224a	187	188	190	183	184
Highest temperature in coal.....°C..	400	400	550	550	550	700	700
Time to reach highest temperature . minutes..	6.7	6.5	7.0	6.5	6.7	6.0	6.0
Tar.....per cent.....			11.5	12.8	10.4	12.0	12.2
Water.....do.....			5.1	4.7	4.8	4.9	4.8
Gas at 25°C.....cubic centimeters..	136	136	975		995	2,005	1,960
Composition of gas: As collected—							
CO ₂	4.6	5.4	3.4	2.9	3.4	2.4	2.4
Illuminants.....	3.8	3.8	6.9	5.7	6.3	7.6	7.1
O.....	1.0	.7	.2	3.5	.4	.1	.1
CO.....	2.7	2.2	4.8	4.0	5.1	7.1	6.6
CH ₄ , C ₂ H ₆ , etc.....	26.3	22.1	47.5	40.0	48.6	35.6	37.8
H.....	2.2	5.7	20.7	18.2	21.0	37.7	36.5
N.....	59.4	60.1	16.5	25.7	15.2	9.5	9.5
Computed to O and N free basis—							
CO ₂	11.6	13.8	4.1	4.1	4.0	2.7	2.7
Illuminants.....	9.6	9.8	8.3	8.1	7.5	8.4	7.9
CO.....	6.8	5.6	5.8	5.6	6.0	7.9	7.3
CH ₄ , C ₂ H ₆ , etc.....	66.4	56.7	57.0	56.5	57.6	39.3	41.7
H.....	5.6	14.1	24.8	25.7	24.9	41.7	40.4
Value of n in C _n H _{2n+2}	1.53	1.79	1.28	1.25	1.24	1.22	1.16

GENERAL SUMMARY.

The investigations described in this bulletin contribute data on the composition of the volatile products from different kinds of coal as evolved at different temperatures. The comparatively large amounts of inert constituents such as CO₂ and water in the products from certain western coals; the large amounts of higher methane hydrocarbons, such as ethane, in the products at moderate temperatures, particularly from the Appalachian coals; and the larger amounts of gas and tarry vapors produced quickly at moderate temperatures from the younger western coals are the main features of the results. The bearing of these results on smoke-producing

tendencies, on studies of the nature of coal substance, and on the calculation of heat value from ultimate analysis is brought out in the foregoing pages. It has been shown that certain bituminous coals of the West are well adapted to the manufacture of a high-grade illuminating gas and of other by-products of coking, notably ammonia.

Any statement as to the character of the gases or volatile products evolved from coal at specified temperatures has little value unless it is accompanied by a clear description of the conditions prevailing and particularly of the points at which temperatures were taken and of the mass of coal which was heated. The temperature varies throughout the mass and is affected by the rate and time of heating. Temperatures outside of the containing vessel produce different temperatures in the coal itself according to the kind of vessel and the time of heating. The distance of the vessel from the point where temperatures are read influences the difference between the observed temperature and that of the coal within the vessel.

It is expected that these investigations will be continued and that the laboratory results will be correlated with experiments on furnaces and gas producers in operation. The work will include the examination of the composition of gases at various points and the study of losses through incomplete combustion. Further laboratory work will be undertaken for the study of the effect of heating the same coal to certain temperatures at different rates, and it is planned to extend the investigation to a greater variety of coals.

ADDENDA.

SMOKE-PRODUCING PRODUCTS OF HEATED POWDERED COAL.

From the experimental data given on pages 32 to 40, the following table has been compiled to show the comparative amounts of smoke-producing volatile products obtained by heating for 10 minutes 10 grams of different coals in powdered form.

TABLE 21.—*Tar and heavy hydrocarbons (smoke producers) obtained at different furnace temperatures, expressed as percentages of coal.*

Coal.	500°	600°	700°	800°	900°
Connellsville, Pa.....		6.5	15.8	18.1	17.5
Zeigler, Ill.....		7.8	9.7	12.2	11.9
Sheridan, Wyo.....	2.1	2.9	10.7	10.7	12.7
Pocahontas, Va.....	.3	1.4	6.7	11.3	9.5

ACCURACY OF GAS ANALYSES.^a

No greater accuracy than 0.2 per cent was attempted in any of the gas analyses, except in the determination of hydrogen in which 0.1 per cent accuracy was obtained. The coal-distillation experiments yielding the gas samples were seemingly incapable of such precision of control as would require any higher degree of accuracy than 0.2 per cent in the gas analysis.

^a See page 22.

PUBLICATIONS ON FUEL TECHNOLOGY.

The following Bureau of Mines publications may be obtained free by applying to the Director, Bureau of Mines, Washington, D. C.:

BULLETIN 1. The volatile matter of coal, by H. C. Porter and F. K. Ovitz. 1910. 58 pp., 1 pl.

BULLETIN 2. North Dakota lignite as a fuel for power-plant boilers, by D. T. Randall and Henry Kreisinger. 1910. 42 pp., 1 pl.

BULLETIN 3. The coke industry of the United States as related to the foundry, by Richard Moldenke. 1910. 32 pp.

BULLETIN 4. Features of producer-gas power-plant development in Europe, by R. H. Fernald. 1910. 27 pp., 4 pls.

BULLETIN 5. Washing and coking tests of coal at Denver, Colo., July 1, 1908, to June 30, 1909, by A. W. Belden, G. R. Delamater, J. W. Groves, and K. M. Way. 1910. 62 pp.

BULLETIN 6. Coals available for the manufacture of illuminating gas, by A. H. White and Perry Barker, compiled and revised by H. M. Wilson. 1911. 77 pp., 4 pls.

BULLETIN 7. Essential factors in the formation of producer gas, by J. K. Clement, L. H. Adams, and C. N. Haskins. 1911. 58 pp., 1 pl.

BULLETIN 8. The flow of heat through furnace walls, by W. T. Ray and Henry Kreisinger. 1911. 32 pp.

BULLETIN 12. Apparatus and methods for the sampling and analysis of furnace gases, by J. C. W. Frazer and E. J. Hoffman. 1911. 22 pp.

BULLETIN 13. Résumé of producer-gas investigations, October 1, 1904, to June 30, 1910, by R. H. Fernald and C. D. Smith. 1911. 393 pp., 12 pls.

BULLETIN 14. Briquetting tests of lignite, at Pittsburgh, Pa., 1908-9, with a chapter on sulphite-pitch binder, by C. L. Wright. 1911. 64 pp., 11 pls.

BULLETIN 16. The uses of peat for fuel and other purposes, by C. A. Davis. 1911. 214 pp., 1 pl.

BULLETIN 18. The transmission of heat into steam boilers, by Henry Kreisinger and W. T. Ray. 1912. 180 pp.

BULLETIN 19. Physical and chemical properties of the petroleums of the San Joaquin Valley, Cal., by I. C. Allen and W. A. Jacobs, with a chapter on analyses of natural gas from the southern California oil fields, by G. A. Burrell. 1911. 60 pp., 2 pls.

BULLETIN 21. The significance of drafts in steam-boiler practice, by W. T. Ray and Henry Kreisinger. 64 pp. Reprint of United States Geological Survey Bulletin 367.

BULLETIN 23. Steaming tests of coals and related investigations, September 1, 1904, to December 31, 1908, by L. P. Breckenridge, Henry Kreisinger, and W. T. Ray. 1912. 380 pp., 2 pls.

BULLETIN 24. Binders for coal briquets, by J. E. Mills. 56 pp. Reprint of United States Geological Survey Bulletin 343.

BULLETIN 27. Tests of coal and briquets as fuel for house-heating boilers, by D. T. Randall. 44 pp., 3 pls. Reprint of United States Geological Survey Bulletin 366.

BULLETIN 28. Experimental work conducted in the chemical laboratory of the United States fuel-testing plant at St. Louis, Mo., January 1, 1905, to July 31, 1906, by N. W. Lord. 51 pp. Reprint of United States Geological Survey Bulletin 323.

BULLETIN 29. The effect of oxygen in coal, by David White. 80 pp., 3 pls. Reprint of United States Geological Survey Bulletin 382.

BULLETIN 30. Briquetting tests at the United States fuel-testing plant at Norfolk, Va., 1907-8, by C. L. Wright. 41 pp., 9 pls. Reprint of United States Geological Survey Bulletin 385.

BULLETIN 31. Incidental problems in gas-producer tests, by R. H. Fernald, C. D. Smith, J. K. Clement, and H. A. Grine. 29 pp. Reprint of United States Geological Survey Bulletin 393.

BULLETIN 32. Commercial deductions from comparisons of gasoline and alcohol tests on internal-combustion engines, by R. M. Strong. 38 pp. Reprint of United States Geological Survey Bulletin 392.

BULLETIN 33. Comparative tests of run-of-mine and briquetted coal on the torpedo boat *Biddle*, by W. T. Ray and Henry Kreisinger. 50 pp. Reprint of United States Geological Survey Bulletin 403.

BULLETIN 34. Tests of run-of-mine and briquetted coal in a locomotive boiler, by W. T. Ray and Henry Kreisinger. 33 pp. Reprint of United States Geological Survey Bulletin 412.

BULLETIN 35. The utilization of fuel in locomotive practice, by W. F. M. Goss. 29 pp. Reprint of United States Geological Survey Bulletin 402.

BULLETIN 36. Alaskan coal problems, by W. L. Fisher. 1911. 32 pp., 1 pl.

BULLETIN 37. Comparative tests of run-of-mine and briquetted coal on locomotives, including torpedo-boat tests, and some foreign specifications for briquetted fuel, by W. F. M. Goss. 58 pp., 4 pls. Reprint of United States Geological Survey Bulletin 363.

BULLETIN 39. The smoke problem at boiler plants, a preliminary report, by D. T. Randall. 31 pp. Reprint of United States Geological Survey Bulletin 334, revised by S. B. Flagg.

BULLETIN 40. The smokeless combustion of coal in boiler furnaces, with a chapter on central heating plants, by D. T. Randall and H. W. Weeks. 188 pp. Reprint of United States Geological Survey Bulletin 373, revised by Henry Kreisinger.

BULLETIN 41. Government coal purchases under specifications, with analyses for the fiscal year 1909-10, by G. S. Pope, with a chapter on the fuel-inspection laboratory of the Bureau of Mines, by J. D. Davis. 1912. 97 pp., 3 pls.

BULLETIN 43. Comparative fuel values of gasoline and denatured alcohol in internal-combustion engines, by R. M. Strong and Lauson Stone. 1912. 243 pp., 3 pls.

BULLETIN 49. Smoke abatement and city smoke ordinances, by S. B. Flagg. 1912. 55 pp.

BULLETIN 55. The commercial trend of the producer-gas power plant in the United States, by R. H. Fernald. 1913. 93 pp., 1 pl.

TECHNICAL PAPER 1. The sampling of coal in the mine, by J. A. Holmes. 1911. 18 pp.

TECHNICAL PAPER 2. The escape of gas from coal, by H. C. Porter and F. K. Ovitz. 1911. 14 pp.

TECHNICAL PAPER 3. Specifications for the purchase of fuel oil for the Government, with directions for sampling oil and natural gas, by I. C. Allen. 1911. 13 pp.

TECHNICAL PAPER 5. The constituents of coal soluble in phenol, by J. C. W. Frazer and E. J. Hoffman. 1912. 20 pp., 1 pl.

TECHNICAL PAPER 8. Methods of analyzing coal and coke, by F. M. Stanton and A. C. Fieldner. 1912. 21 pp.

TECHNICAL PAPER 9. The status of the gas producer and of the internal-combustion engine in the utilization of fuels, by R. H. Fernald. 1912. 42 pp.

TECHNICAL PAPER 10. Liquefied products from natural gas; their properties and uses, by I. C. Allen and G. A. Burrell. 1912. 23 pp.

TECHNICAL PAPER 16. Deterioration and spontaneous combustion of coal in storage, a preliminary report, by H. C. Porter and F. K. Ovitz. 1912. 14 pp.

TECHNICAL PAPER 20. The slagging type of gas producer, with a brief report of preliminary tests, by C. D. Smith. 1912. 14 pp., 1 pl.

TECHNICAL PAPER 25. Methods for the determination of water in petroleum and its products, by I. C. Allen and W. A. Jacobs. 1912. 13 pp.

TECHNICAL PAPER 26. Methods of determining the sulphur content of fuels, especially petroleum products, by I. C. Allen and I. W. Robertson. 1912. 13 pp.

TECHNICAL PAPER 31. Apparatus for the exact analysis of flue gas, by G. A. Burrell and F. M. Seibert. 1913. 12 pp.

TECHNICAL PAPER 36. The preparation of specifications for petroleum products, by I. C. Allen. 1913. 12 pp.

TECHNICAL PAPER 37. Heavy oil as fuel for internal-combustion engines, by I. C. Allen. 1913. 36 pp.

